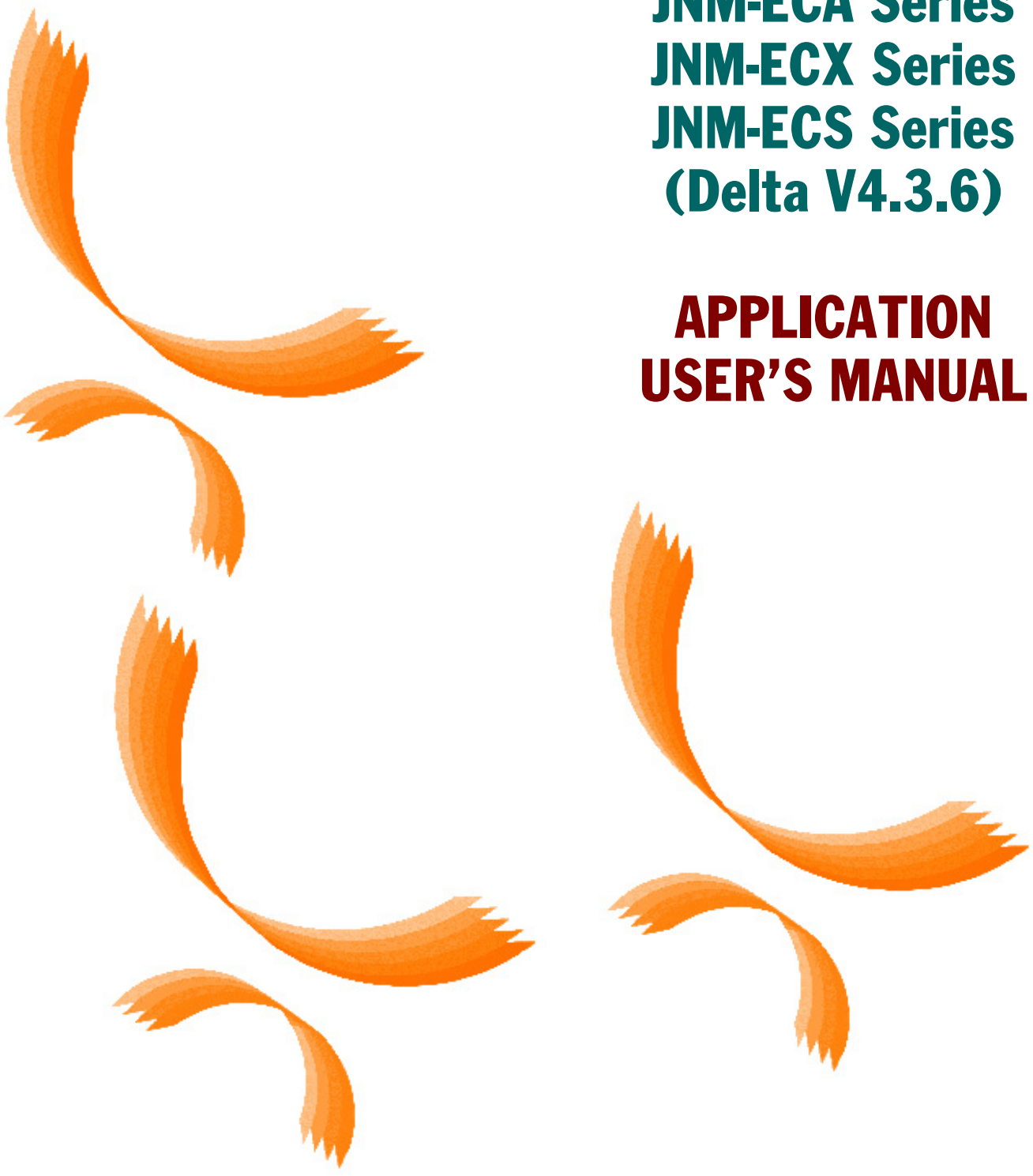
JNM-ECA Series
JNM-ECX Series
JNM-ECS Series
(Delta V4.3.6)

APPLICATION USER'S MANUAL



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JNM-ECA Series
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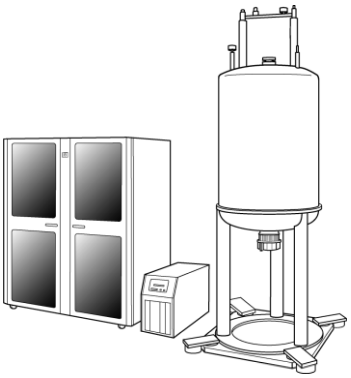
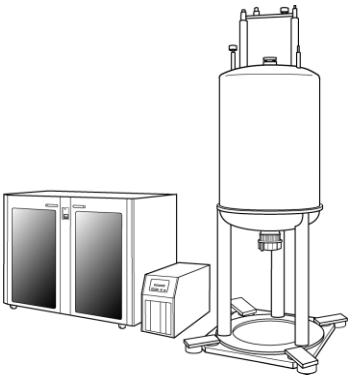
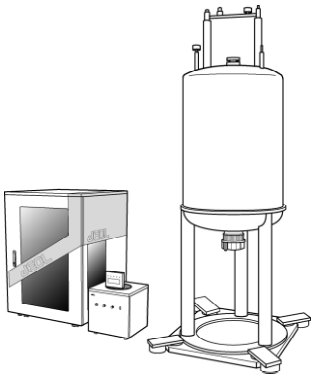


JNM-ECA Series



JNM-ECX Series



JNM-ECS Series

This manual explains how to perform more-advanced measurement using the JNM-ECA, JNM-ECX or JNM-ECS Series FT NMR system.

Please be sure to read this instruction manual carefully, and fully understand its contents prior to the operation or maintenance for the proper use of the instrument.

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NOTATIONAL CONVENTIONS AND GLOSSARY

General notations

– CAUTION – :	Points requiring great care and attention when operating the device to avoid damage to the device itself.
✍:	Additional points to remember regarding the operation.
☞:	A reference to another section, chapter or manual.
1, 2, 3 :	Numbers indicate a series of operations that achieve a task.
◆ :	A diamond indicates a single operation that achieves a task.
Reference:	Useful information for you.
File:	The names of menus, commands, or parameters displayed on the screen are denoted with **bold** letters.
File–Exit :	Selecting a menu item from a pulldown menu is denoted by linking the menu and the item with a dash (–). For example, **File–Exit** means selecting **Exit** from the **File** menu.
Ctrl :	Keys on the keyboard are denoted by enclosing their names in a box.

Mouse terminology

Mouse pointer:	A mark, displayed on the screen, which moves following the movement of the mouse. It is used to specify a menu item, command, parameter value, and other items. Its shape changes according to the situation.
Click:	To press and release the left mouse button.
Right-click:	To press and release the right mouse button.
Double-click:	To press and release the left mouse button twice quickly.
Drag:	To hold down the left mouse button while moving the mouse.

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1.1 RELAXATION TIME MEASUREMENT

There are three kinds of relaxation times, T_1, $T_{1\rho}$, and T_2.
Section 1.1 explains the method of T_1 measurement, which is frequently performed.

1.1.1 Relaxation Time (T_1) Evaluation

To obtain T_1 with high accuracy, array measurement is performed using the variable of recovery times. To set the variable of recovery times to appropriate values, the approximate T_1 of the sample must be determined first.
This section describes the method of a simple T_1 evaluation by means of inversion recovery.

■ Simple T_1 evaluation method using T_1 measurement mode by means of inversion recovery

If a peak changes as a single exponential function, the observed magnetization $M(\tau)$ is expressed as a function of the relaxation delay time τ by using the inversion recovery method:

$$M(\tau) = M_0 \{1-2\exp(-\tau/T_1)\}$$

From this equation it is found that T_1 can be evaluated from the delay time when the observed magnetization becomes zero. This delay time is called the null point, and is represented by τ_{null}.
Thus, T_1 is given by

$$T_1 = \tau_{null} / \ln 2 = 1.44 \times \tau_{null}$$

To obtain an accurate value of T_1, first obtain the null point, and then perform the array measurement.

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1.1.2 Measurement of Relaxation Times (T_1)

■ To obtain the null point

1. Tune the probe.
2. Verify the 90° pulse width.

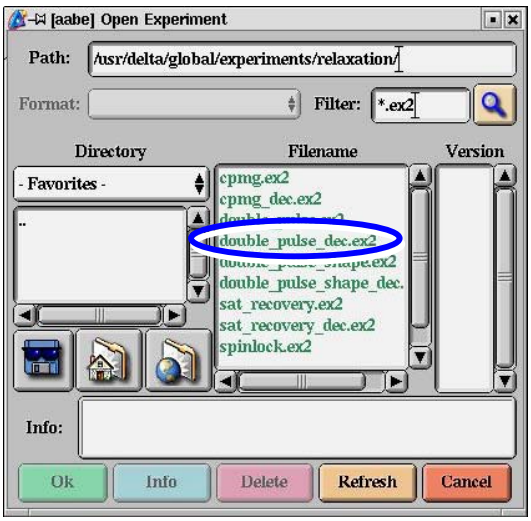
   To enhance accuracy of T_1 measurement, verify the 90° pulse width of the sample used to measure relaxation time. To do this, perform array measurement in the **single pulse** or **single pulse dec** measurement mode**.**
3. Click on the **Expmnt** button in the **Spectrometer Control** window.

   The **Open Experiment** window opens.
4. Click on **relaxation**.

Fig. 1.1 Open Experiment window

5. To perform T_1 measurement for ^{1}H, select **double_pulse.ex2** from the file name list box.

   To perform T_1 measurement for ^{13}C, select **double_pulse_dec.ex2**.



The **Experiment Tool** window used to set the parameters opens.

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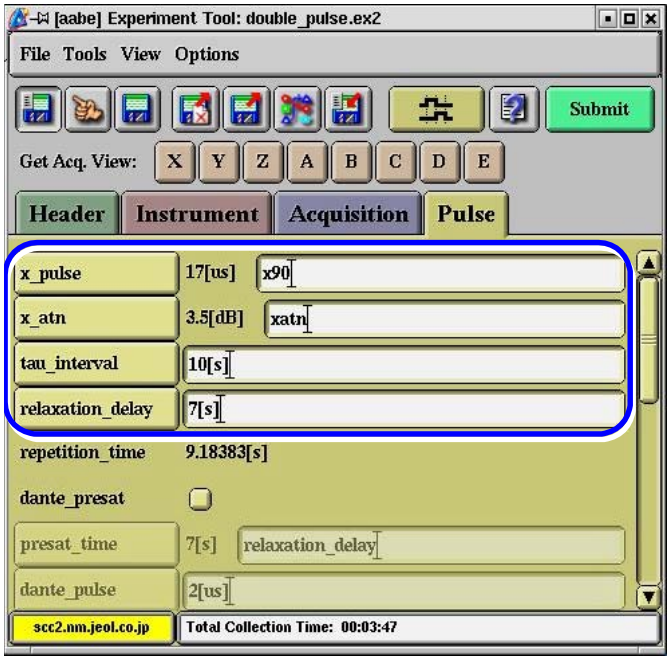
6. Enter the following values.

x_ pulse 90° pulse width obtained in Step 2
tau_interval Value at most 1/10 of the expected T_1 as an initial value
relaxation_delay Value at least 5 times the expected T_1



7. Click on the **Submit** button.

Measurement is carried out.

8. Perform data processing in the **1D processor** window, and adjust the phase on the phase correction panel in the **1D processor** window to turn the peak downward.

9. Increase **tau_interval** in the **Experiment Tool** window, and perform measurement again.

Perform the phase correction on the obtained spectrum using the same phase correction values as those obtained in Step 8.

While you repeat this operation, the peak reverses and then turns upward. During the process, the **tau_interval** at the time when the peak disappears is obtained. This is the null point. You can obtain an approximate value of T_1 by multiplying the null point by 1.4.

■ Setting the parameters

1. After you obtain the null point, enter the approximate value of T_1 multiplied by 10 into relaxation_delay.

The peaks in the spectrum have different T_1 values. However, enter 10 times the maximum T_1 value in the peaks used for the T_1 measurement.

2. Based on the obtained approximate value of T_1, set **tau_interval** to array parameter (array variable).

To enter the array parameter for T_1 measurement by the inversion recovery method, be sure to array the values in order from the greatest value. The arrow buttons

switch between the selection of ascending and descending order as shown in Fig. 1.2.

Set the initial value of the array parameter (maximum value) to the approximate value of T_1 multiplied by 10, corresponding to infinite tau in the inversion recovery.

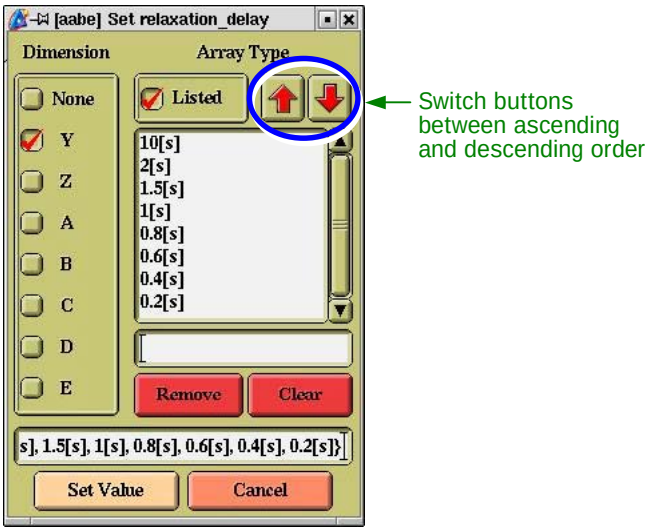


Fig. 1.2 Array parameter window

3. Click on the **Set Value** button.

The array parameter window closes, and the set values are entered into **tau_interval** in the **Experiment Tool** window.

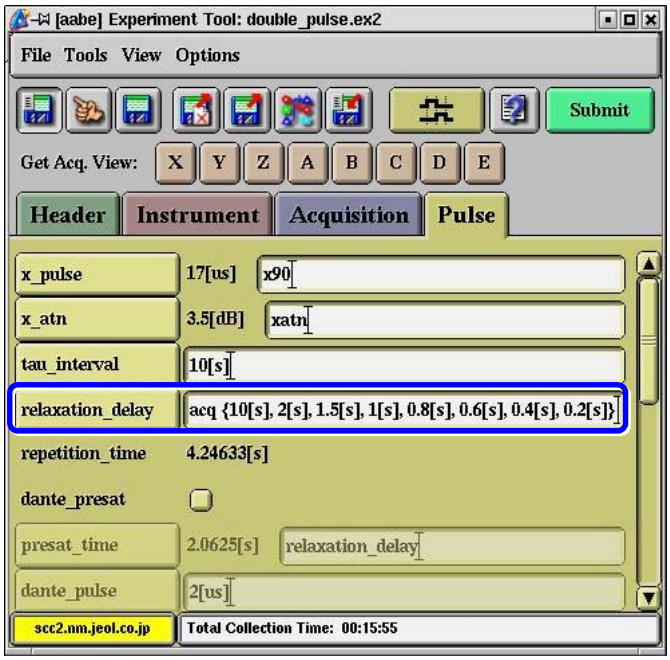


Fig. 1.3 Experiment Tool window

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1.2 RELAXATION TIME DATA PROCESSING

Data processing following measurement is performed in the **nD processor** window, and then T_1 calculation is performed in the **Curve Analysis** window. Chapter 2 explains the procedure for data processing.

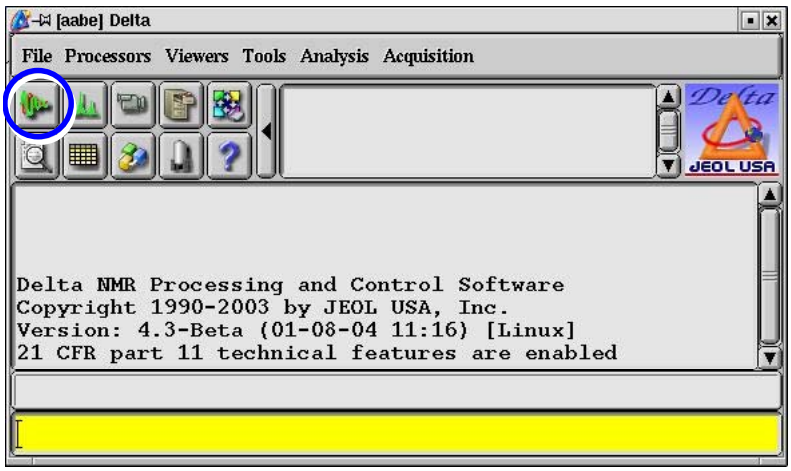
1.2.1 Loading Relaxation Time Measurement Data

First, load measurement data in the **nD Processor** window in the same way as to perform 2D measurement data processing.

If measurement data was transferred from the spectrometer immediately after relaxation time measurement finished, and the **nD Processor** window is already open, you can omit the procedure of Section 1.2.1.

To load relaxation time measurement data (FID) in the **nD Processor** window,

1. Click on the **Data Processor** button in the **Delta Console** window.


[aabe] Delta
File Processors Viewers Tools Analysis Acquisition
JEOL USA
Delta NMR Processing and Control Software
Copyright 1990-2003 by JEOL USA, Inc.
Version: 4.3-Beta (01-08-04 11:16) [Linux]
21 CFR part 11 technical features are enabled

The **Open Data for Processing** window is displayed.

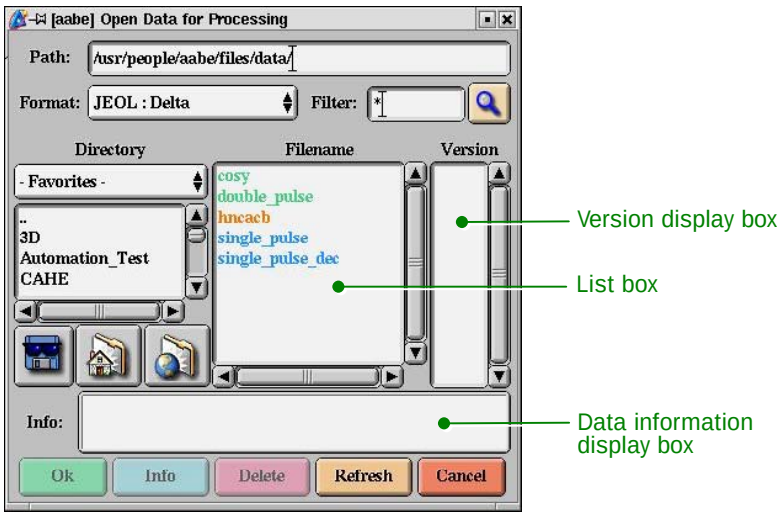


Fig. 1.4 Open Data for Processing window

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2. Click on the data file you want to load from the list box.

The following data information with the latest version is displayed in the data information display box.

The T_1 data obtained in the array measurement is represented as having 2D format.

3. If the Time domain/Frequency domain display in the data information display box is not [s] (time domain data), select the version number from the version display box so as to display the time domain data.

If the Time domain/Frequency domain display in the data information display box displayed in Step 2 is Time domain, that is, the latest version is time domain data (FID data), the selection of the version can be omitted.

4. Click on the **Ok** button.

The **nD Processor** window opens.

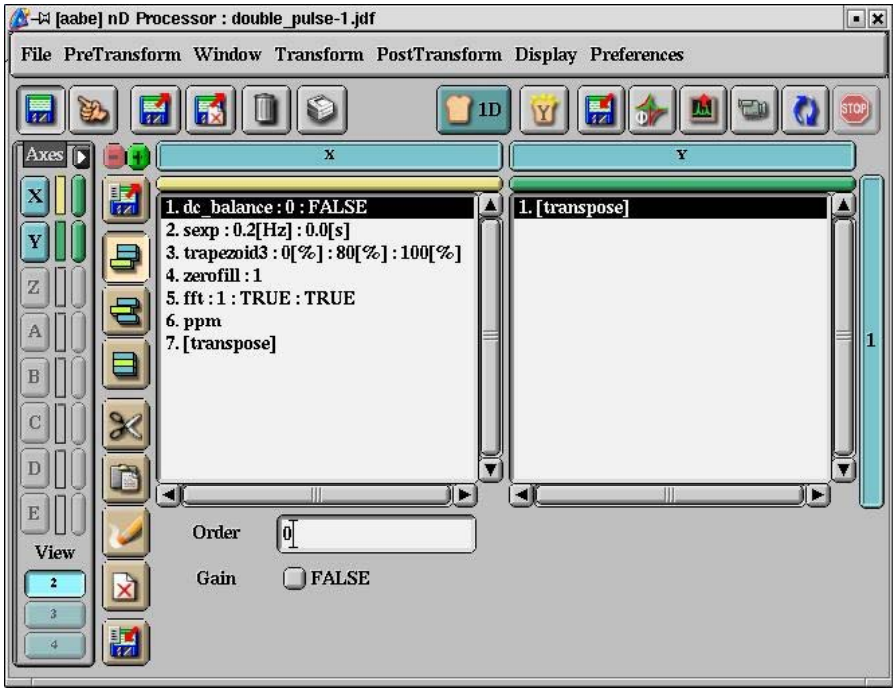

Fig. 1.5 nD Processor window

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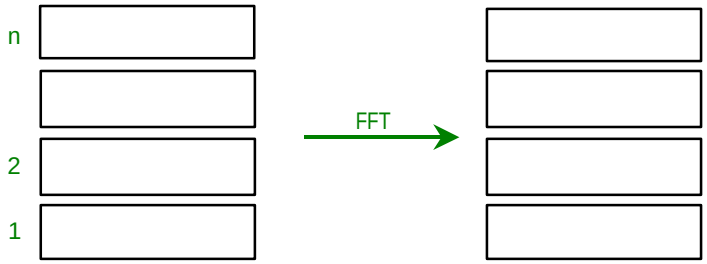
1.2.2 Processing Relaxation Time Measurement Data

Processing of relaxation time measurement data is performed in the following three steps.

Step 1

All sets of measurement data from the first to the nth are transformed together under the same condition.



Step 2

The processed data sets are transferred to the **Curve analysis** window. Then, the peak for T_1 calculation is selected from any numbered data set by peak picking.

Step 3

The relaxation times are obtained by approximate calculation.

The procedures are next explained in the order of the above steps.

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1.2.2a Fourier-transforming (Step 1)

- **If an appropriate window function and phase correction values are already known and are saved in the processing list**

1. Load the desired processing list in the **nD Processor** window.

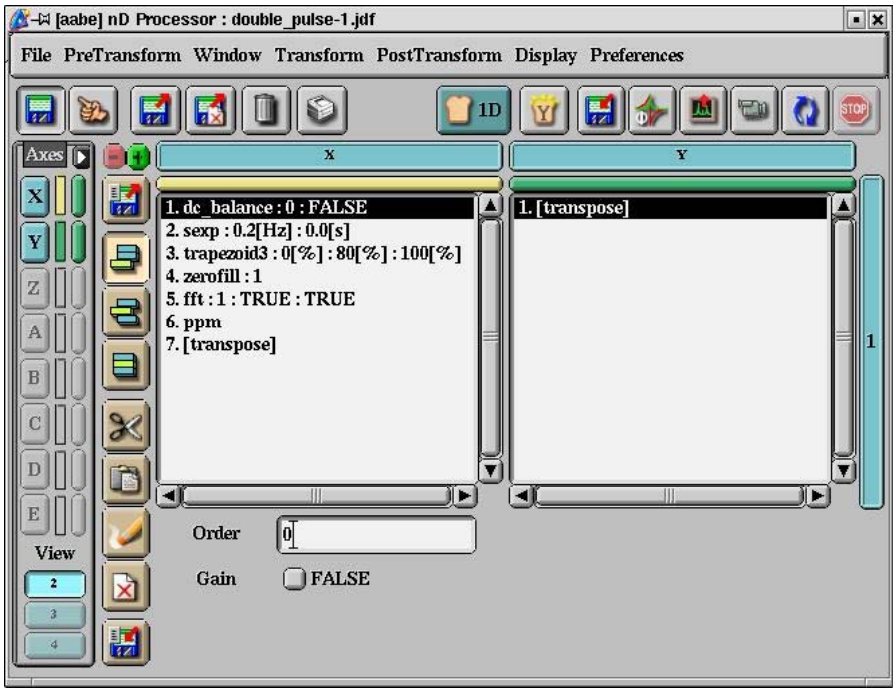

Fig. 1.6 nD Processor window

2. Click on either of the **Process File And Put In Data Slate** button or **Process File And Put In Data Slate** button.

Normally, click on the button.

Clicking on the button performs the data processing specified in the processing list for the first to the nth measurement data sets, and displays the processed data sets in the **Data Slate** window.

Clicking on the button performs the data processing specified in the processing list for the first to the nth measurement data sets, and displays the processed data sets in the **Data Viewer** window.

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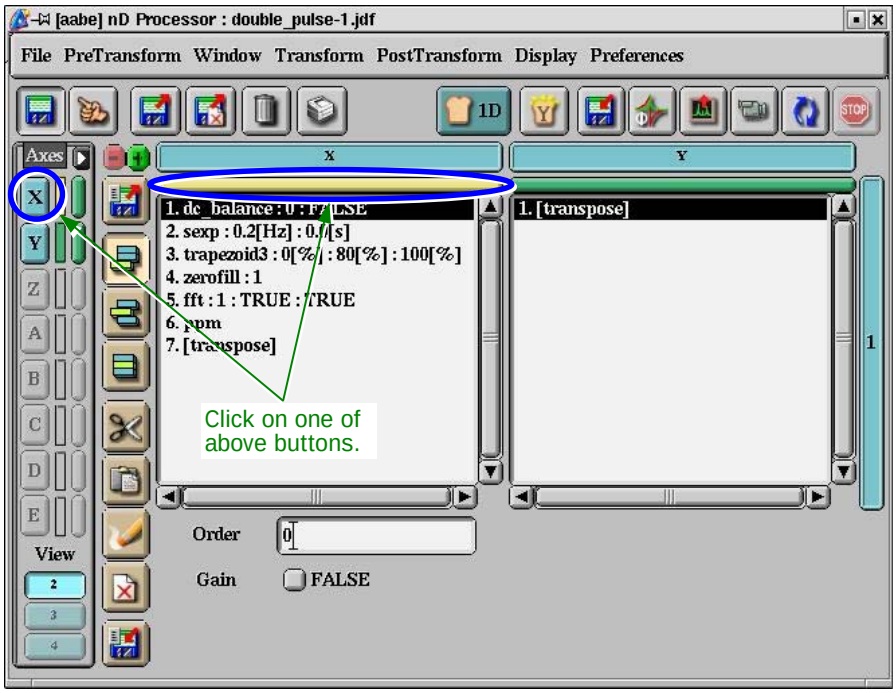
- **If an appropriate window function and phase correction values are not known**

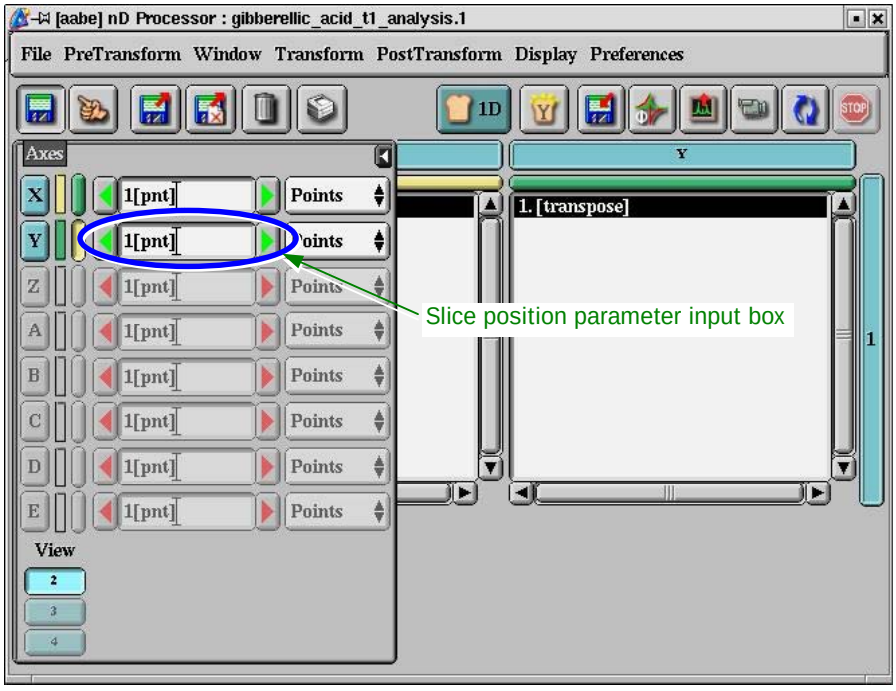
  Display a set of relaxation time measurement data as 1D slice data in the **1D Processor** window, and obtain an appropriate window function and phase correction values by following Step 1 to 6 below; then process and display the data according to Step 7.

  1. Click on the **X** button in the **nD Processor** window.



  2. Click on the **Axes** button to display the slice position setting screen, and set the slice data to the number of points from the number of sets (1 - n) in the relaxation time measured data.

  Normally, slice the first set of measurement data as it is easy to correct its phase.



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3. Click on the 1D Slice **1D Slice** button.

The slice data at the specified position is displayed in the **1D Processor** window.

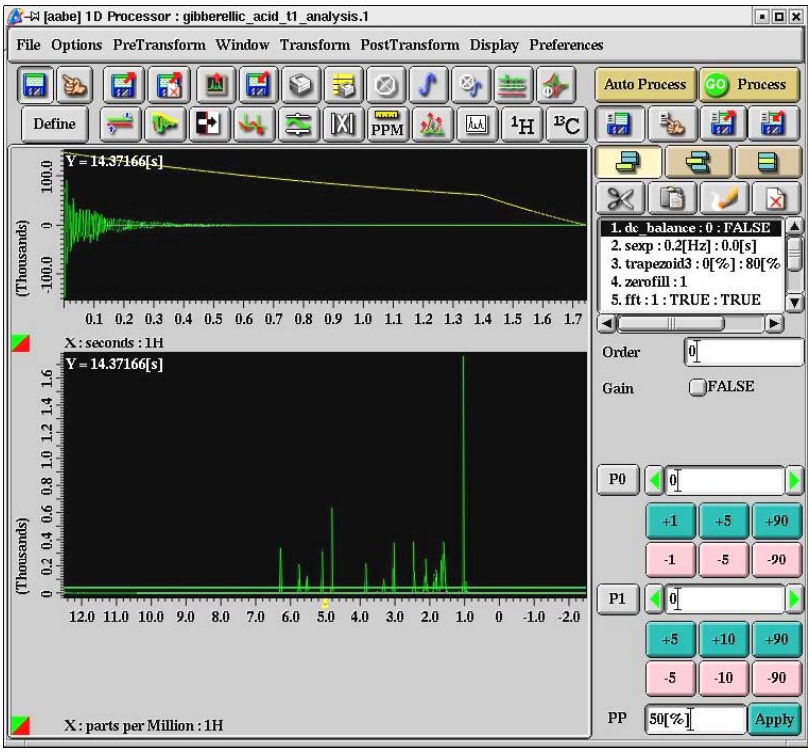

Fig. 1.7 1D Processor window

4. Change the window function and its parameter values, and enter an appropriate window function condition.

This operation is the same as that of changing the ordinary 1D data window function.

5. Carry out phase correction, and obtain the appropriate phase correction values.

This operation is the same as that of correcting the phase of the ordinary 1D data.

- Be sure to perform manual phase correction without using automatic phase correction.
- If you cannot correct the phase of the J-modulated and J-coupled peak during T_2 measurement, refer to the topic labeled Reference below.

6. Close the**1D Processor** window.

The window function condition and the phase correction values obtained in Steps 4 and 5 are automatically inserted in the processing list in the ***nD Processor*** window.

7. Click on the **Process File And Put In Data Slate** button or **Process File And Put In Data Viewer** button

Normally, click on the button.

Clicking on the button performs the data processing specified in the processing list for the first to the nth measurement data sets, and displays the processed data sets in the ***Data Slate*** window.

Clicking on the button performs the data processing specified in the processing list for the first to the nth measurement data sets, and displays the processed data sets in the **Data Viewer** window.

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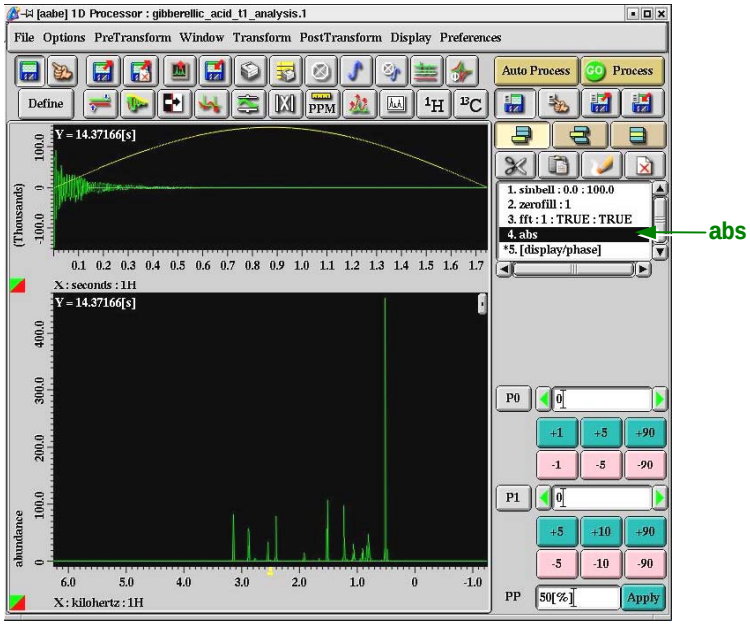
Reference: If you cannot correct the phase of T_2 (transverse relaxation time) measurement data

Repeat Step 4 using the **sinbell** window function. Perform power processing without phase correction in Step 5 according to the following procedure:

a. Click on the **Append** button in the**1D Processor** window.

b. Select **PostTransform**–**Abs** from the menu bar.
The power processing step **abs** is entered in the processing list.



c. Proceed to Step 6.

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1.2.2b Selecting a peak (Step 2)

To perform this operation, the relaxation time measurement data after Fourier transformation should first be loaded in the **Curve Analysis** window.

■ To open the Curve Analysis window

◆ Select **Viewers–Analysis–Curve Analysis** from the menu bar in the **Delta Console** window.

The **Curve Analysis** window opens.

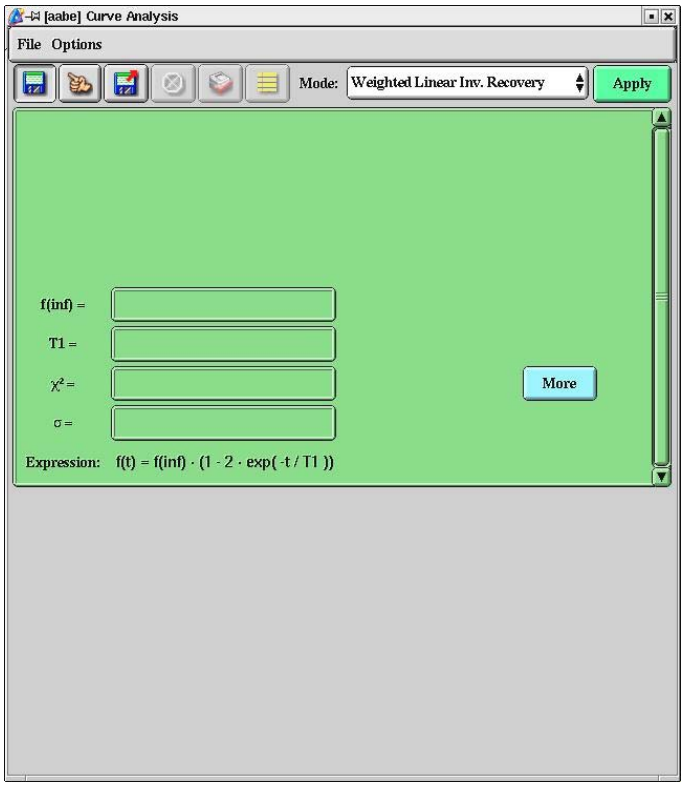


Fig. 1.8 Curve Analysis window

■ To load relaxation time measurement data after Fourier transformation in the Curve Analysis window

- **If relaxation time measurement data after Fourier transformation is saved on a hard disk**

1. Click on the **Get Data From File** button in the **Curve Analysis** window.
2. Click on the **Open Data File** button.

   The **Open File** window opens.

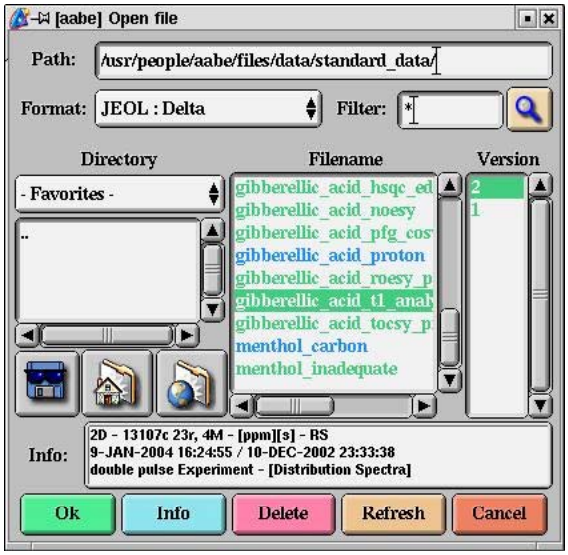
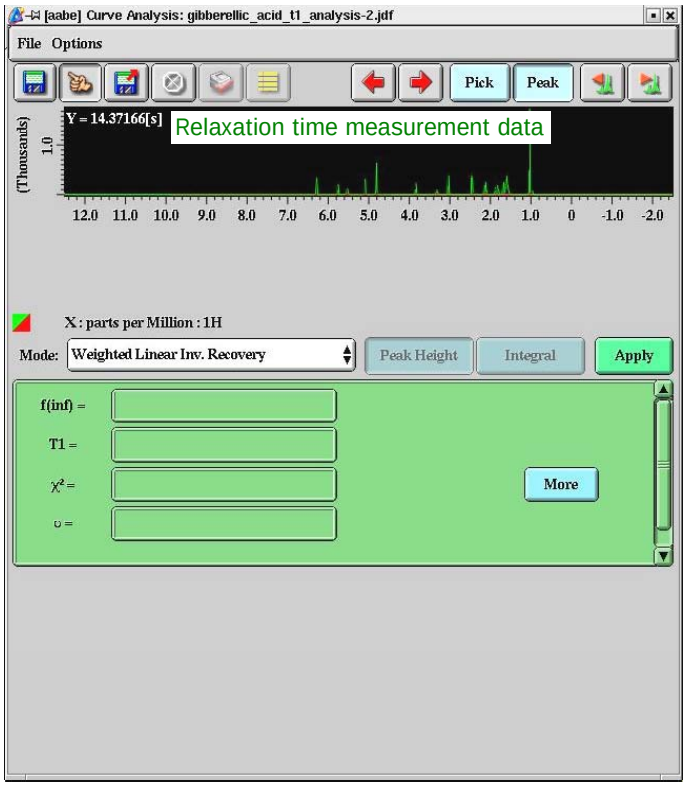


Fig. 1.9 Open File window

3. Select the file, in which the relaxation time measurement data after a Fourier transformation is saved, from the list box in the **Open File** window, and then click on the **Ok** button.

The selected relaxation time measurement data is loaded in the **Curve Analysis** window.



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- **If relaxation time measurement data after a Fourier transformation is being displayed**

1. Click on the **Open Data By Fingering a Geometry** button in the **Data Slate** window.
2. Click on the **Open Data File** button.
   The mouse pointer changes to the shape of a finger.
3. Move the mouse pointer to the area in which the relaxation time measurement data after Fourier transformation is displayed, and click on it.
   The selected relaxation time measurement data is loaded in the **Curve Analysis** window.

To select a peak

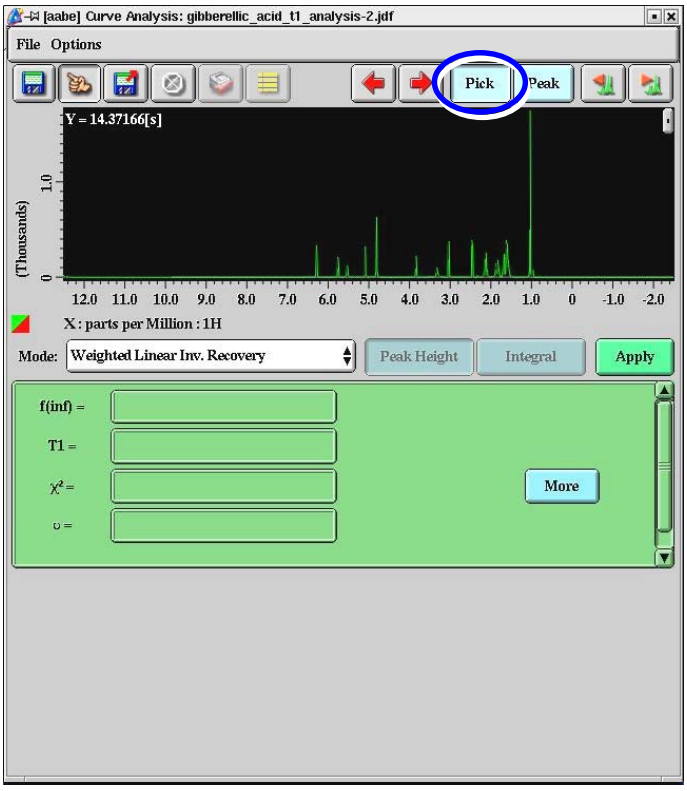
Either the **Pick** mode or the **Peak** mode is used to select a peak.

If there are a lot of peaks for T_1 measurement, and you want to print all those T_1 values, the **Peak** mode is useful. The peaks to be used in the **Peak** mode must be listed in the peak picking list.

The **Pick** mode can be used to obtain T_1 at any position of a spectrum. The top of the peak is not required for T_1 calculation in the **Pick** mode, making it different from the **Peak** mode.

- **To select a peak in the Pick mode**

1. Click on the **Pick** button in the **Curve Analysis** window.
   The cursor tool bar in the spectral display area changes to the **Pick** mode.



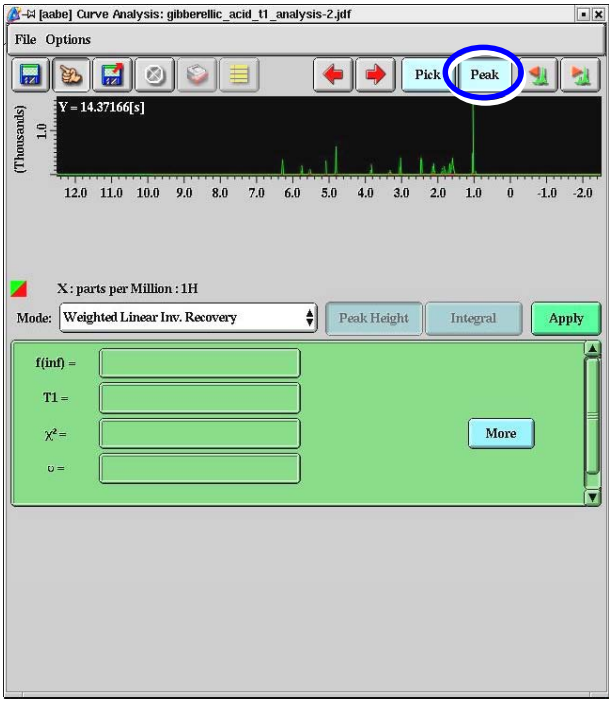
2. Click on the **Pick position** button in the cursor tool **Pick** mode.

3. Move the mouse pointer onto the X ruler in the spectral display area, and press and hold the left mouse button.
   The cursor is displayed.

4. With the mouse button pressed, move the cursor to the top of the peak whose relaxation time you want to obtain, and release it.
   The pick position marker is displayed at the position at which you released the mouse button.

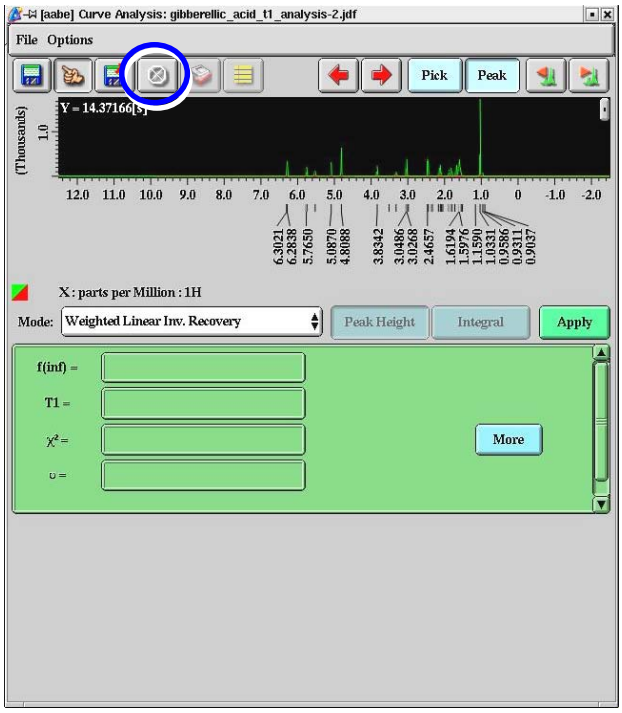
- **To select a peak in the Peak mode**

1. Click on the **Peak** button in the **Curve Analysis** window.



2. Click on the **Peak Pick** button.
   Peak picking is carried out.
   If required, before picking peak, change threshold level and noise level so that small signals or peaks having fine splitting, which T_1 value does not need, may not be picked up.

C I



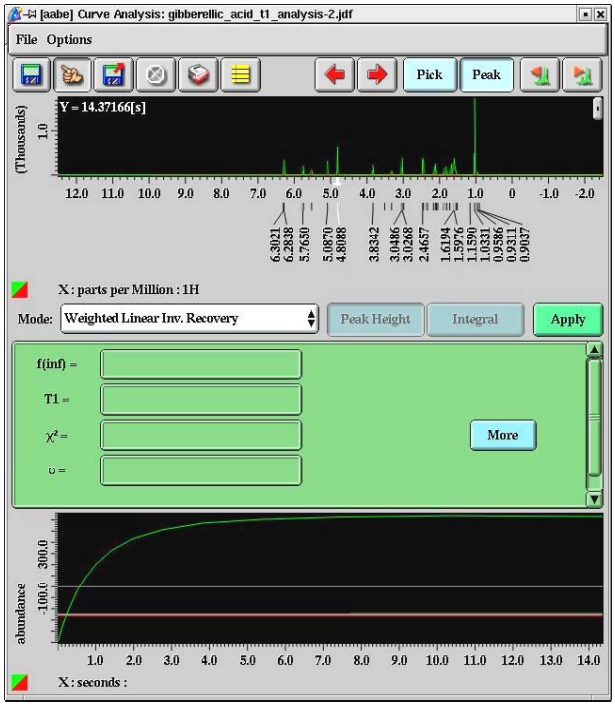
3. Click on the **Select** button in the cursor tool **Peak** mode.

4. Move the mouse pointer onto the X ruler of the spectrum display range, press and hold down the left mouse button.

The curser appears.

5. Move the cursor to the position which crosses to the top of the peak to obtain the current relaxation time, and release the mouse button.

A peak position mark appears at the position at which the mouse button was released.



The selected peak values change to yellow, and a peak intensity table is created. When printing out the T_1 values of two or more signals collectively, drag cursor around the peak area. All peaks listed up by peak picking in the area are selected, and numerical markers become white.

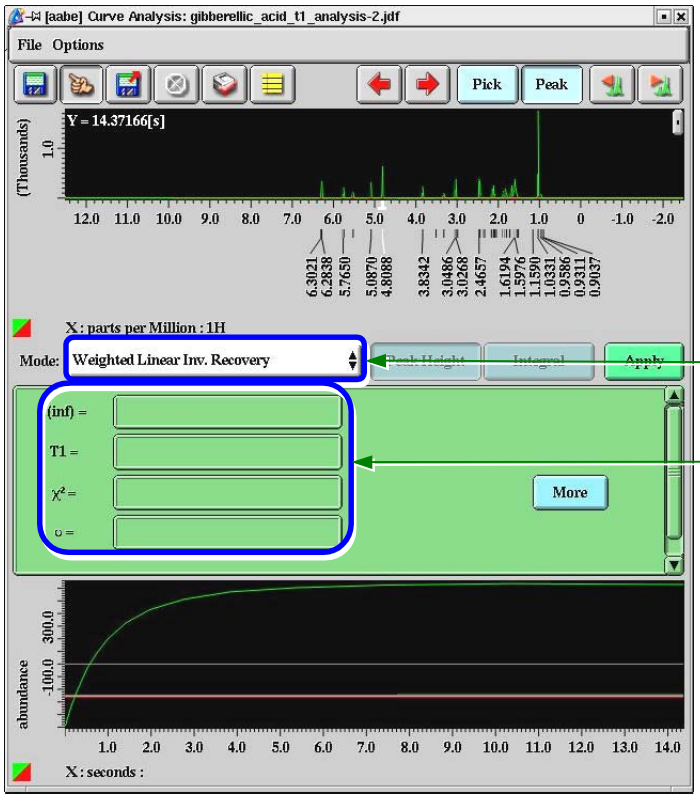
C I

1.2.2c Obtaining relaxation times by approximate calculation (Step 3)

■ To select an approximate calculation equation

◆ Select the desired approximate calculation equation in the approximate calculation equation selection box.

The selected approximate calculation equation is displayed in the approximate calculation equation display box.


[aabe] Curve Analysis: gibberellic_acid_t1_analysis-2.jdf
File Options
Pick
Peak
Y = 14.37166[s]
(Thousands)
1.0
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
6.3021 6.2838 5.7650 5.0870 4.8088 3.8342 3.0486 3.0268 2.4657 1.6194 1.5976 1.1590 1.0331 0.9586 0.9311 0.9037
X : parts per Million : 1H
Mode:
Weighted Linear Inv. Recovery
Approximate calculation equation selection box
(inf) =
T1 =
χ² =
υ =
More
Approximate calculation equation display box
abundance
300.0
-100.0
1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0
X : seconds :

approximate calculation equation	Description
Weighted Linear	Weighted linear least squares method Lower weights are applied to measurement points having higher **tau_interval** values.
Unweighted Linear	Unweighted linear least squares method
Nonlinear	Nonlinear least squares method

✍ The statement, such as Inv. Recovery, Sat. Recovery, and Spin Lock, which follows these commands shows experimental method. Inv. Recovery, Sat. Recovery, and Spin Lock are meaning Inversion Recovery method, Saturation Recovery method, and Spin Lock method, respectively.

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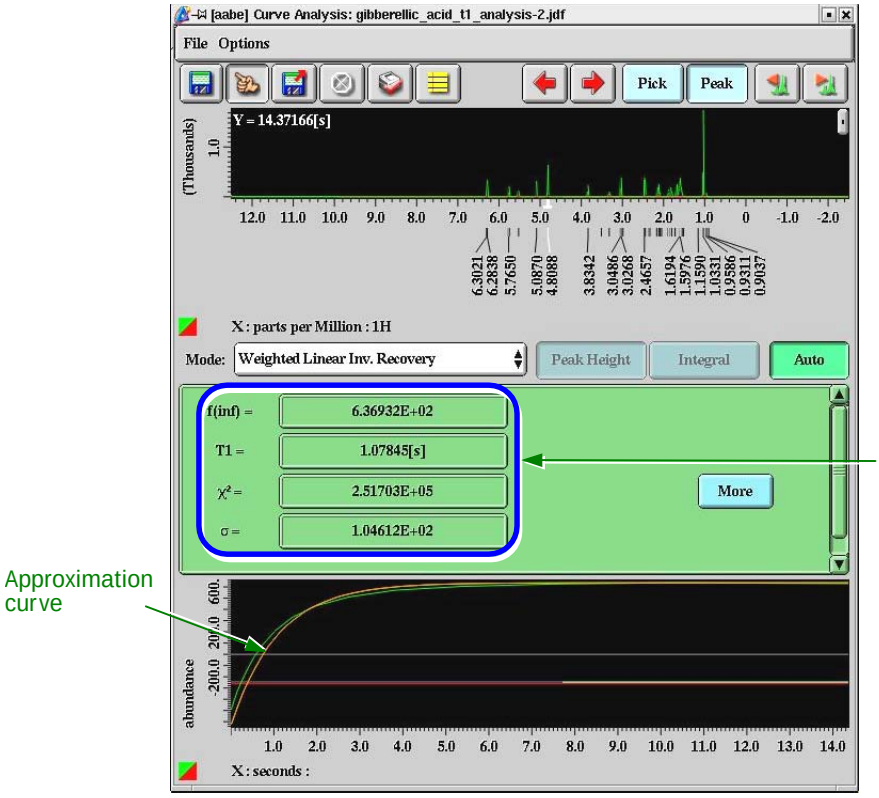
To execute an approximate calculation and obtain relaxation times

- Click on the **Apply** button.

  The approximate calculation is executed, and the calculated result of the relaxation time and the yellow approximation curve are displayed.



When we enter the selection state by pressing the **Apply** button, the display changes to **Auto**. When changing the peak to obtain a relaxation time or when changing selection of an approximate calculation formula, an approximate calculation is performed automatically.

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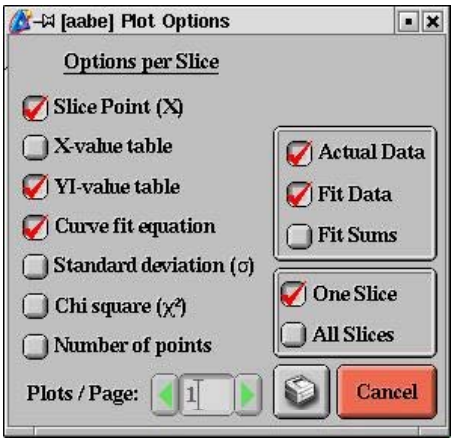
1.2.3 Plotting Calculation Results

1. Click on the **Plot Data File** button in the **Curve Analysis** window.
Items and buttons for plotting are displayed in the approximation curve display area.
The **Plot Option** window opens.



2. Put a check mark on the buttons with the items you want to plot.
To print the T_1 values of more than one peak selected in the **Peak** mode together, click on the **All Slices** button.

3. Click on the **Plot data with current state** button.
The items that were selected in Step 2 are plotted.

2

MEASUREMENT OF DIFFUSION COEFFICIENT AND DATA PROCESSING

2.1 METHOD OF EVALUATING DIFFUSION COEFFICIENT 2-1
2.2 HOW TO MEASURE PFG STRENGTH 2-2
2.3 MEASUREMENT OF DIFFUSION COEFFICIENT (D) 2-4
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2.4.2a Fourier transformation (Step 1) 2-11
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2.1 METHOD OF EVALUATING DIFFUSION COEFFICIENT

Generally, diffusion is a process by which the concentration of solution or temperature of a sample approaches uniformity. However, here “diffusion” means self-diffusion, in which a molecule changes the position in solution or in solid state. Therefore, the diffusion coefficient is a measure of transfer of the molecule.

■ Method of evaluating diffusion coefficient by NMR

Although the translational motion of molecule is 3-dimensional motions, the translational motion actually observed by NMR is only the motion parallel to the z axis because a magnetic field gradient is applied along the z axis.

If the translational molecular motion is a random walk, the probability of the molecule moving a distance Δz from its initial position during time t is the following Gaussian function.

$$P(\Delta z, t) = (4\pi Dt)^{1/2} \exp(-\Delta z^2 / 4Dt)$$

where D is the diffusion coefficient of the molecule. In this function, the Δz distributes wide range with increasing t.

In PFG NMR, the transverse magnetization produced by a 90°pulse is in the state (coherent) where the phase is complete in the beginning. If PFG is applied here, since the spin receives a magnetic field strength corresponding to its z coordinate, the phase of the magnetization changes with the magnetic field strength. If the strength of the magnetic field gradient is G, the duration of the field gradient pulse is δ, and the gyromagnetic ratio is γ, the final amplitude of phase modulation is $\Phi = \gamma G \Delta z \delta$ for a square-wave field gradient in the direction of z axis. The distribution function of the phase modulation is as follows.

$$P(\Phi, t) = (4\pi Dt)^{-1/2} (\gamma G\delta)^{-1/2} \exp(-\Phi^2 / 4(\gamma G\delta)^2 Dt)$$

Therefore, when the coherence is reestablished due to rephasing by a second PFG after vanishing due to dephasing by the first PFG, the signal intensity is as follows if the time between the two FG pulses is Δ:

$$I(G, \Delta) = I(0, \Delta) \exp(-D(\gamma G\delta)^2 \Delta)$$

Furthermore, when the influence of the diffusion between FG pulses cannot be disregarded, it is corrected as follows.

$$I(G, \Delta) = I(0, \Delta) \exp(-D(\gamma G\delta)^2 (\Delta - \delta / 3))$$

Therefore, the diffusion coefficient D can be evaluated from the formula by changing either the strength of the magnetic field gradient G, the duration of the field gradient pulse δ, or the time between the two magnetic-field-gradient pulses Δ.

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2.2 HOW TO MEASURE PFG STRENGTH

In order to obtain the diffusion coefficient, it is necessary to measure the strength of magnetic-field gradient G. Therefore, the maximum magnetic-field-gradient strength of the system being used should be measured before carrying out an actual measurement.

■ Simple way to measure PFG strength

1. Prepare a water sample with the liquid height adjusted to about 5 mm.

✍ A sample tube such as a micro-cell, in which the height of liquid is clearly known, is needed.

2. Click on the **Expmnt** button in the **Spectrometer Control** window.

The **Open Experiment** window opens.

3. Click on **diffusion**.

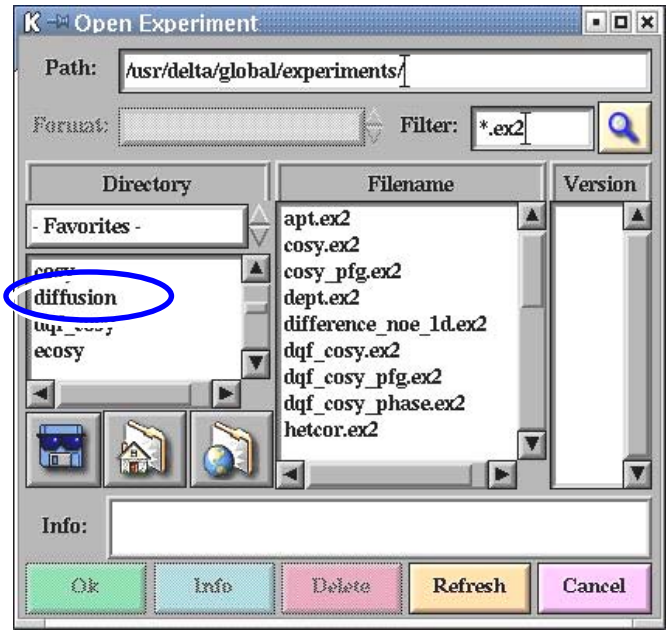

Fig. 2.1 Open Experiment window

4. Select the **fg_power_check.ex2** sequence from the File name list box.

The Experiment Tool window for setting parameters opens.

5. Set the parameter grad_amp.

✍ Since a long magnetic-field-gradient pulse will be used in the **fg_power_check.ex2** sequence, do not use a large magnetic-field gradient. Use a value of 1% to 5% for the value of **grad_amp.**

6. Click on the Submit button.

A measurement is performed.

7. Process the data in the **1D processor** window and display the absolute value of the spectrum.

In order to display the absolute value, perform **abs** processing.

8. Measure the frequency at the both ends of the obtained rectangular spectrum in Hz.

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9. Select **Tools–Math–Gradient Strength** from the menu bar of the **Delta Console** window.

The **Gradient Strength** window opens.

10. Input value into each item of the **Gradient Strength** window.

Select **1H** (Proton) in **Nucleus,** and input the liquid height of the sample used into **Coil length** column. Moreover, input the frequency obtained in step 8 into the **Left position** and **Right position** column.

The obtained magnetic-field-gradient strength is displayed on **Gradient Strength** window.

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2.3 MEASUREMENT OF DIFFUSION COEFFICIENT (D)

As discussed above, the measurement of the diffusion coefficient can be carried out by changing either the field-gradient strength G, the duration of gradient pulse δ, or the time between two FG pulses Δ.
However, in the measurement in which a time parameter such as the duration of the field gradient pulse δ or time between FG pulses Δ changes, you have to take into account the influences time, such as relaxation. Therefore, the measurement by changing magnetic-field-gradient strength G is presently in general use. The procedure for measurement of the diffusion coefficient by changing the magnetic-field-gradient strength G is explained below.

■ To obtain measurement conditions

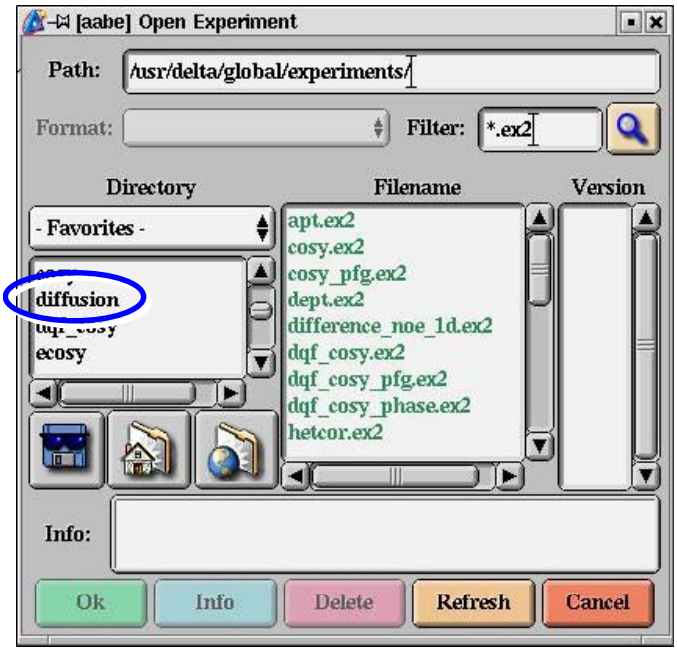
1. Stop the sample spinning, and tune the probe.

2. Check the 90° pulse width.

In order to improve the accuracy of the diffusion coefficient measurement, we recommend that you check the 90° pulse width of the sample you are measuring. For checking the 90° pulse, perform an array measurement using the measurement mode **single_pulse.ex2** or **single_pulse_dec.ex2**.

3. Click on the **Expmnt** button in the **Spectrometer Control** window.
The **Open Experiment** window opens.

4. Click on **diffusion**.



5. Select the desired sequence from the File name list.
The **Experiment Tool** window for setting up parameters opens.

6. Input the following value if needed.
The values of **x_pulse** and **gradient_max** of the following are recalled automatically from the default values in the probe file. Input values when values obtained in step 2 differ from the values in the probe file.

x_pulse: 90°pulse width which you obtained in step 2.
gradient_max: The maximum magnetic field strength [T/m] in the system currently used.

For the maximum magnetic field strength, input into **gradient_max**, measure the value for every system combination of the probe and the maximum output of the FG power supply referring to section 2.2 "How to measure PFG strength".

7. Input values for the parameters of measurement of the diffusion coefficient.

The following three parameters are necessary for measuring the diffusion coefficient.

diffusion_time: Interval of two FG pulses (diffusion time Δ).
grad_1: Duration of magnetic-field-gradient pulse.
grad_1_amp: Magnetic-field strength (G).

The duration of magnetic-field-gradient pulse (δ) which is used for calculation of the diffusion coefficient is not equivalent to the parameter **grad_1** in some sequences. Refer to the parameter **delta** for the duration of the magnetic-field-gradient pulse (δ) used for the calculation of the diffusion coefficient.

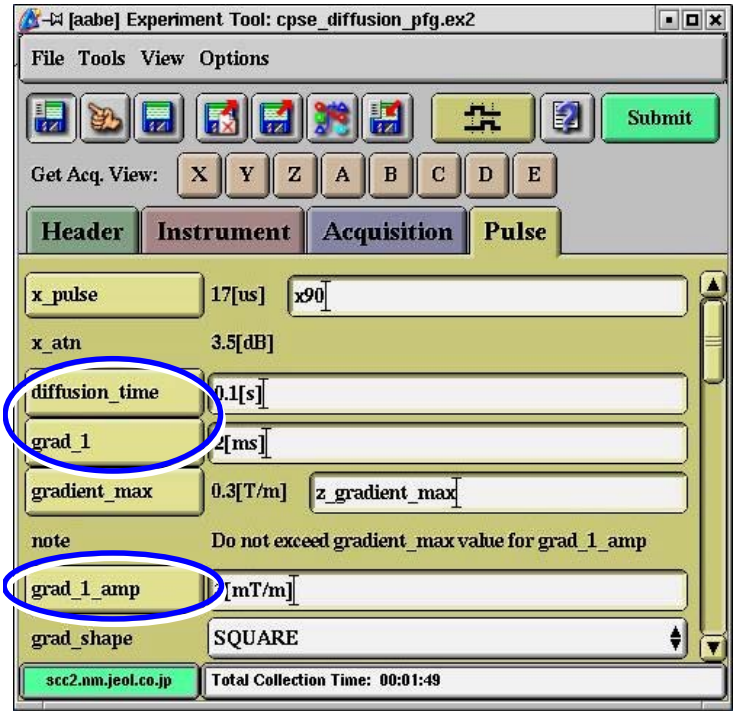


Fig. 2.2 Experiment Tool window

8. Input a number about 10 times the value of T_1 into **relaxation_delay**.

9. Perform an array measurement at the minimum value and maximum of the variable magnetic-field strength that are used in the actual measurement.

For example, to change magnetic field gradient from 3 mT/m to 0.27 T/m, carry out an array measurement at 3 mT/m and 0.27 T/m.

The instrument cannot output a magnetic field strength greater than **gradient_max**.

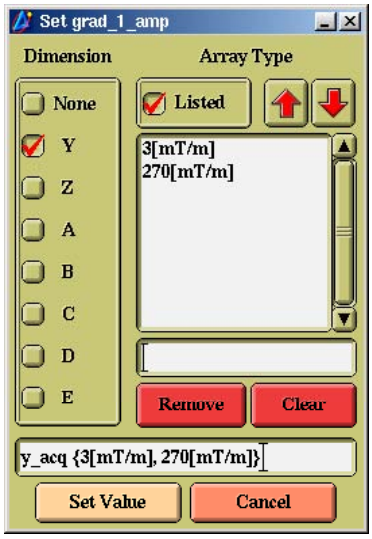
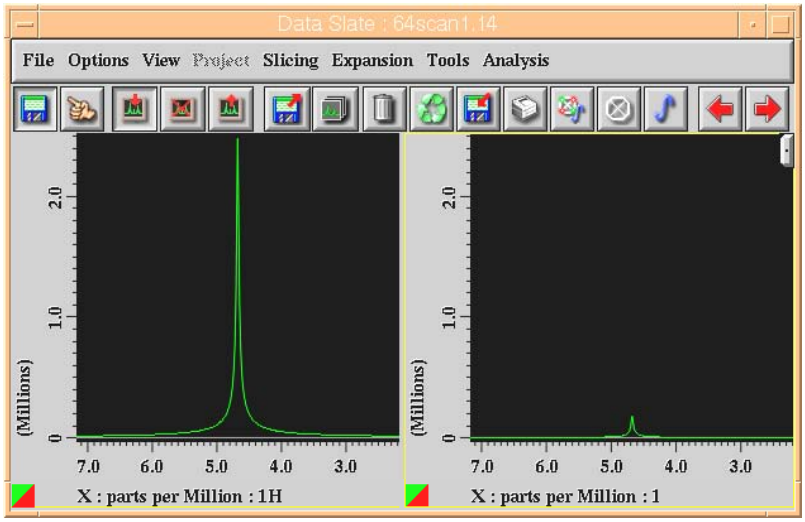


Fig. 2.3 Array parameter window

10. Process the data in the **nD processor** window, and check the decay of the signal.
Repeat steps 8 and 9, changing the values of **diffusion_time** and **grad_1** so that the decay ratio of the signal may become in the range of 10:1 to 20:1 for the maximum and minimum of field gradient strength.



■ Measurement of diffusion time

1. Stop sample spinning, and adjust tuning of the probe.

2. Check the 90°pulse width.

In order to improve the accuracy of the diffusion coefficient measurement, we recommend you to check the 90° pulse width of the sample to measure. To check the 90° pulse, perform an array measurement in the **single_pulse.ex2** or **single_pulse_dec.ex2** measurement mode.

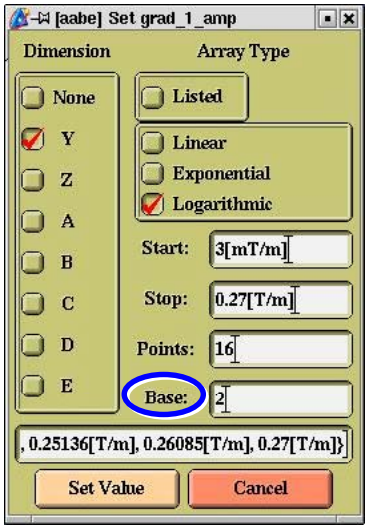
3. Set up the various parameters obtained in the procedure "■To obtain measurement conditions".

Set up **scans** so that you obtain a sufficient S/N ratio also for the decay signal.

C I

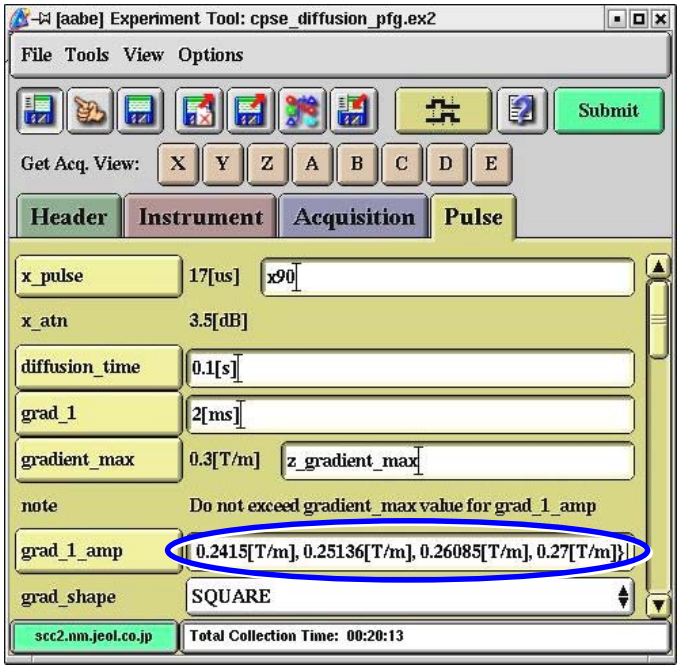
4. Set **grad_1_amp** to a suitable array variable in the range of the minimum and minimum value of the variable magnetic-field gradient used in the condition setting.

In measurement of a diffusion coefficient, good measurement can be performed changing an array variable so that the 2nd power of the magnetic field gradient may be measured at equal intervals. For this reason, the array variable can be easily set by selecting **Logarithmic** as an **Array Type** and by setting the **Base** value to 2.



5. Click on the **Set Value** button.

Close the array parameter window, and input the set values into the **Experiment Tool** window.



6. Click on the **Submit** button.

Measurement starts.

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2.4 PROCESSING DIFFUSION MEASUREMENT DATA

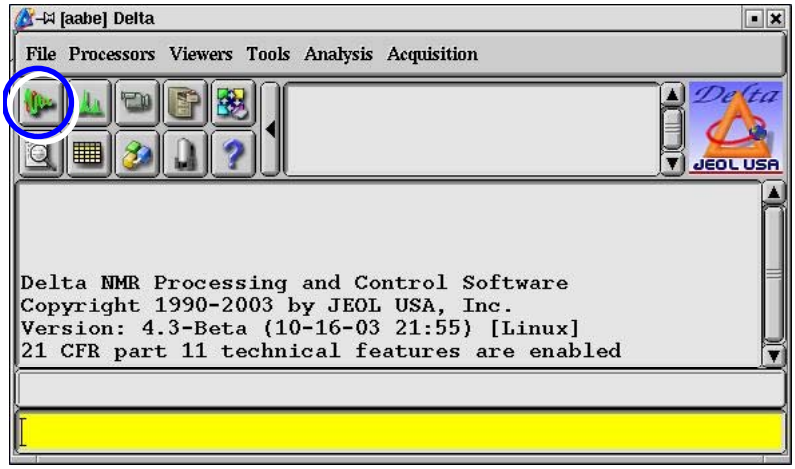
After measurement, process the data in **nD Processor** window, and use the **Curve Analysis** window for calculation of the diffusion coefficient. The procedure is explained below.

First, recall the measurement data into the **nD Processor** window as in two-dimensional measurement data processing. In addition, the operation of section 2.4.1 is not necessary when the **nD Processor** window is already displayed when measurement data is transmitted from the spectrometer immediately after the end of diffusion-coefficient measurement.

2.4.1 Loading Diffusion Coefficient Measurement Data

In order to load the diffusion coefficient measurement data (FID) into the **nD Processor** window, perform the following procedure.

1. Click on the **Data Processor** button in the **Delta Console** window.


[aabe] Delta
File Processors Viewers Tools Analysis Acquisition
JEOL USA
Delta NMR Processing and Control Software
Copyright 1990-2003 by JEOL USA, Inc.
Version: 4.3-Beta (10-16-03 21:55) [Linux]
21 CFR part 11 technical features are enabled

The **Open Data for Processing** window appears.

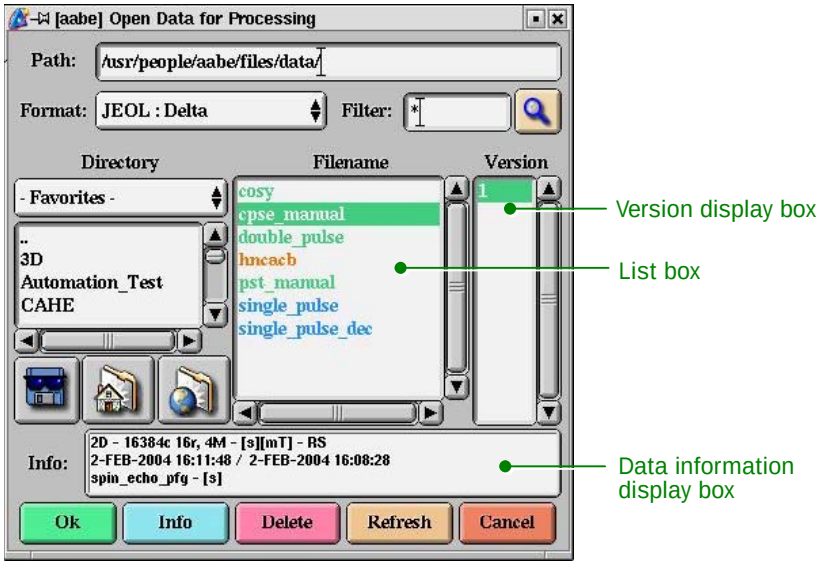


Fig. 2.4 Open Data for Processing window

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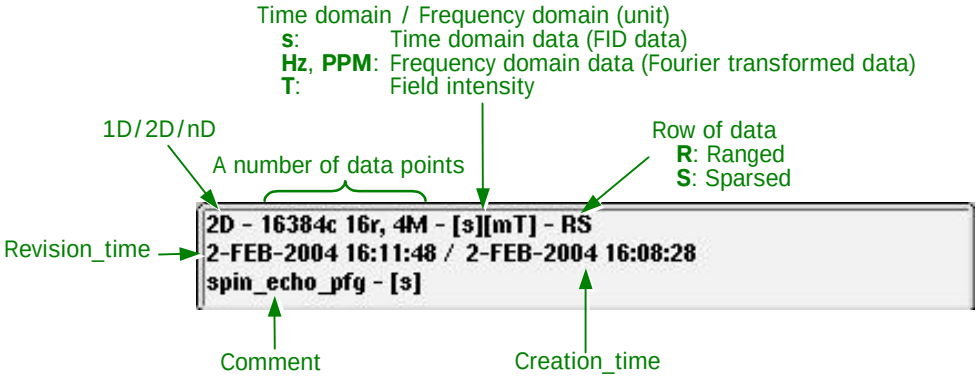
2. Click the data file in the filename list box.

In the data information display box, the data information of the newest version is displayed as shown below. Note that the format of the data obtained by the array measurement is displayed as 2D.



3. Looking at the data information display box, and select the version of stored FID from the version display box.

If the newest version of the data displayed in step 2 is the time domain data (FID data), selection of a version is unnecessary.

4. Click on the **Ok** button.

The **nD Processor** window opens.

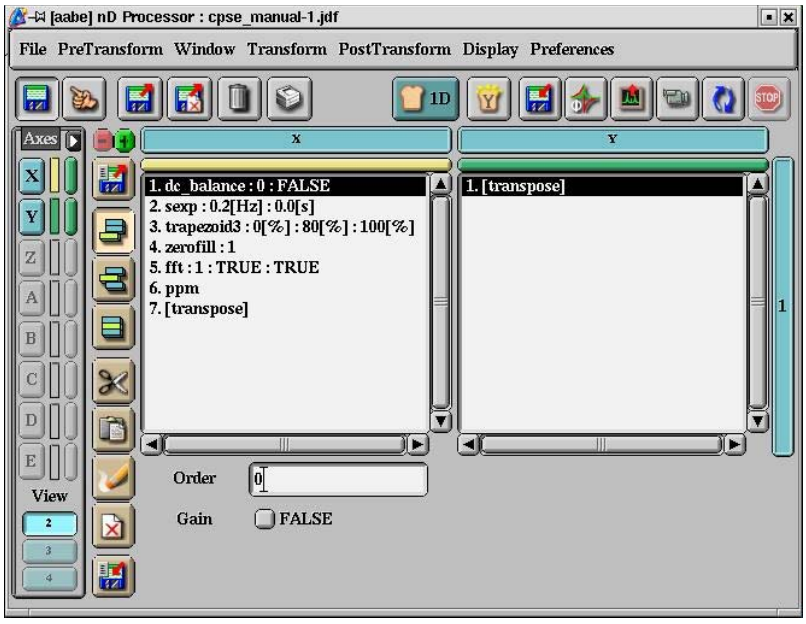


Fig. 2.5 nD Processor window

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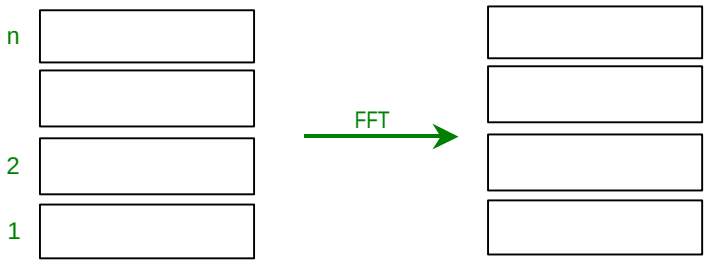
2.4.2 Procedure for Processing Diffusion Coefficient Measurement Data

The processing of the diffusion coefficient measurement data consists of the following three steps.

Step 1

Fourier-transform the diffusion measurement data sets under the same conditions for the 1 to n-th measurement data set as shown in the following schematic figure.



Step 2

Transmit the processed data to the **Curve Analysis** window. Then, select the peaks to use to perform the diffusion coefficient calculation by picking the peaks.

Step 3

Obtain the diffusion coefficient using the approximate calculation.

The procedure is explained in the order of these step.

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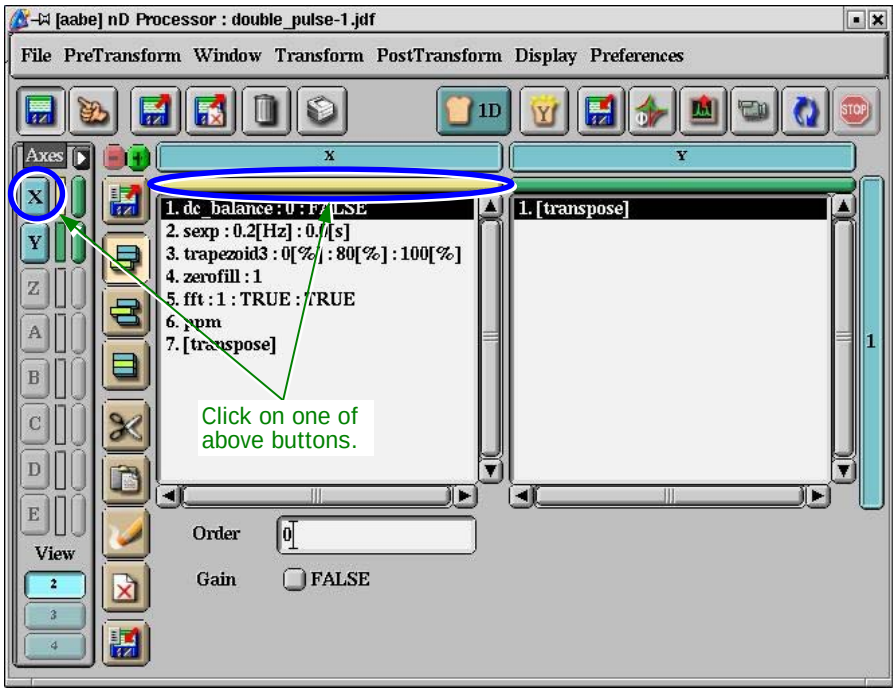
2.4.2a Fourier transformation (Step 1)

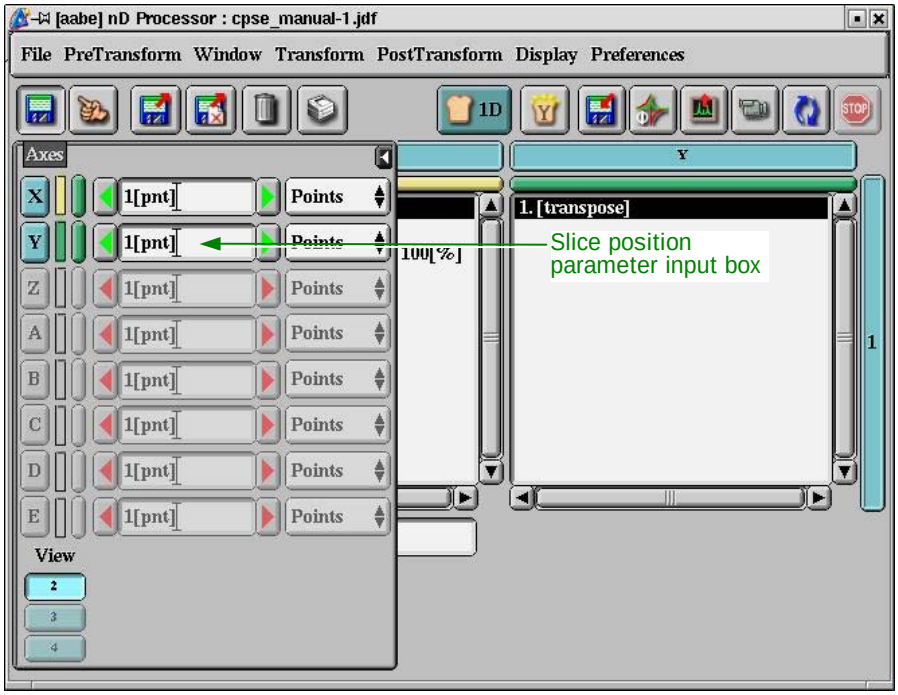
Displaying one diffusion coefficient measurement data set in the **1D Processor** window as 1-dimensional slice data, search a suitable window function and phase correction value.

1. Click on the **X** button in the **nD Processor** window.



2. Click on the **Axes** button to display the slice position setting screen, and set the slice data to the number of points from the number of sets (1 - n) in the diffusion coefficient measurement data.

Usually, slice the first measurement data, whose phase correction is easy to carry out easily.



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3. Click on the 1D Slice 1 D Slice button.

The slice data at the specified position is displayed on the **1D Processor** window.

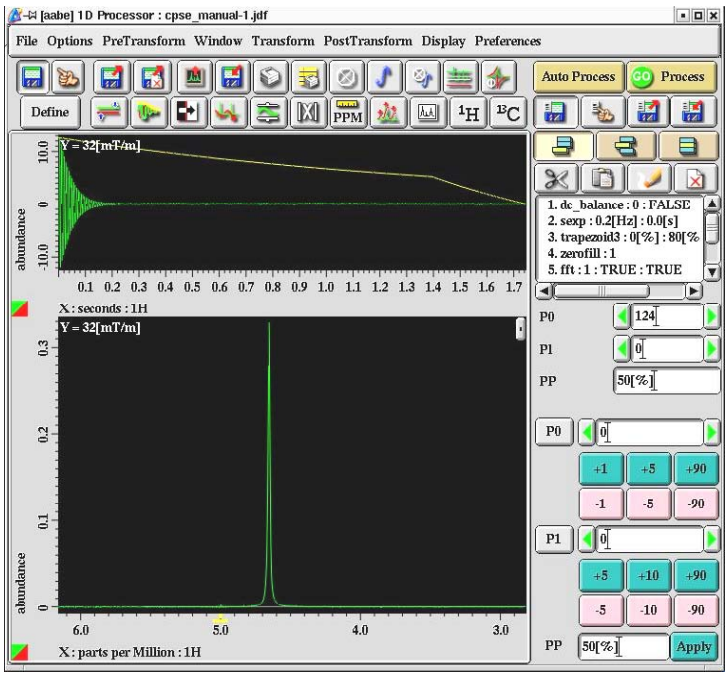


Fig. 2.6 1D Processor window

4. Set up suitable window function conditions, changing the window function and parameter value.

The operation of changing the window function is the same as that of usual 1D data. When calculating the diffusion coefficient, only the height information of a peak is required. Therefore, in order to reduce the contribution of noise, it is more effective to use a wider window function than usual.

5. Correcting the phase manually, obtain suitable phase-correction value.

The operation of phase correction is the same as that of the usual 1D data.

- Be sure to correct phase manually without using automatic phase correction.
- The phase of a peak having J coupling may not be corrected due to J modulation. If that happens, refer to the following procedure "Reference: When the phase of measurement data can not be corrected."

6. Close the **1D Processor** window.

The window function conditions and phase-correction values which were obtained in steps 4 and 5 are automatically entered in the process list of the **nD Processor** window.

7. Click on one of the following icon.

Usually select **Process File And Put In Data Slate** button or **Process File And Put In Data Viewer button.**

If you click the button, the after performing the data processing specified by the process list to the 1 to n-th measurement data set, the ***Data Slate*** window appears.

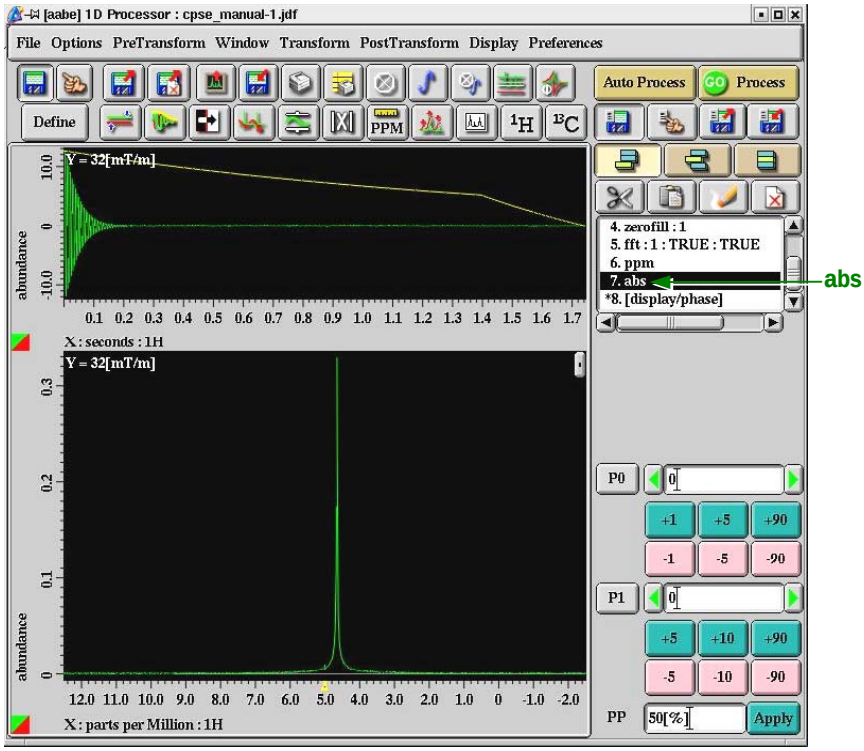
If you click the button, the after performing the data processing specified the process list to the 1 to n-th measurement data sets, the ***Data Viewer*** window appears.

- **Reference: When the phase of measurement data cannot be corrected**

  Power processing replaces phase correction in step 5.
  Perform the following operational procedure.

  a. Click on the **Append** button in the **1D Processor** window.

  b. Select **Post Transform–Abs** in the menu bar.
  The **abs** function for power processing is entered into the process list.



  c. Go to step 6.

C I

2.4.2b Extraction of peaks, and creation of peak-intensity table (Step 2)

This operation calls the diffusion coefficient measurement data that performed Fourier transform processing to the **Curve Analysis** window, and change the **Mode** to **Diffusion Analysis**.

■ Open the Curve Analysis window and change the Mode

1. Select **Viewers–Analysis–Curve Analysis** in the menu bar of for **Delta Console** window.

The **Curve Analysis** window opens.

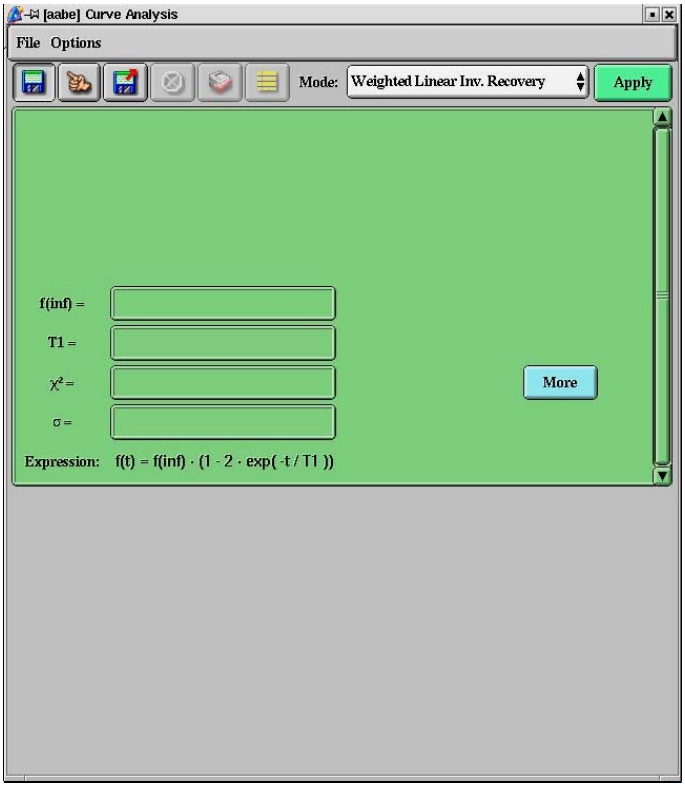
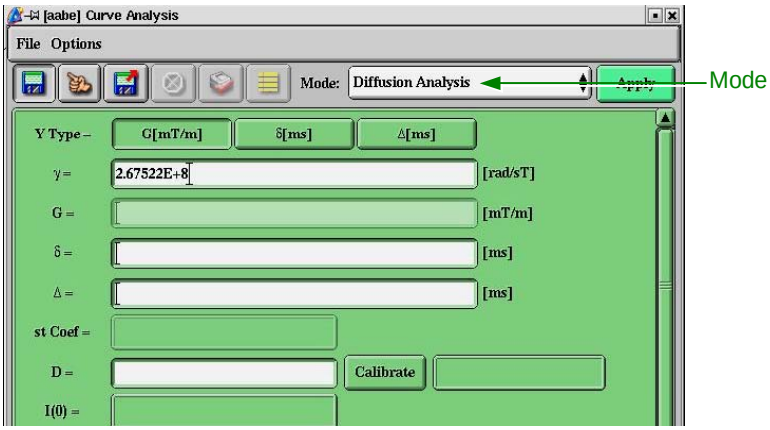


Fig. 2.7 Curve Analysis window

2. Change the **Mode** to **Diffusion Analysis**.

The window changes to the **Diffusion Analysis** mode.



C I

Reading the data Fourier transformed in the Curve Analysis window

When Fourier transformated diffusion coefficient measurement data is saved on the hard disk

1. Click on the **Get Data From File** button in the **Curve Analysis** window.
2. Click on the **Open Data File** button.
   The **Open File** window opens.

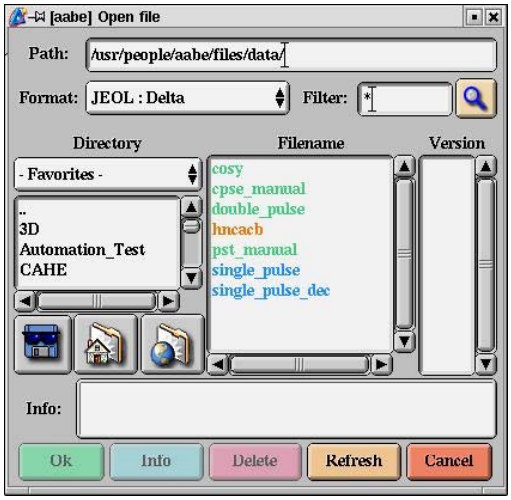
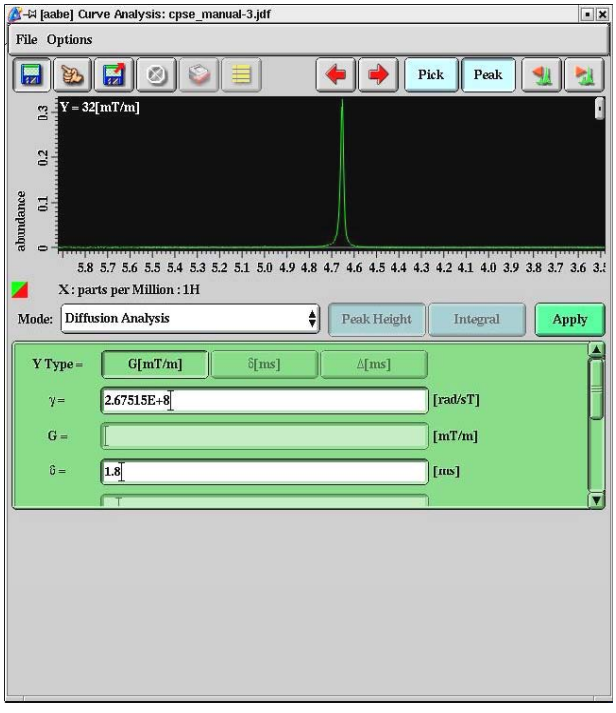


Fig. 2.8 Open File window

3. Select the file containing the Fourier transformed diffusion coefficient measurement data from the list box of in the **Open File** window, and click on the **Ok** button.
   The selected diffusion coefficient measurement data is loaded into the **Curve Analysis** window.



C I

- **When Fourier-transformed diffusion coefficient measurement data is displayed**

1. Click on the **Open Data By Fingering a Geometry** button in the **Data Slate** window.
2. Click on the **Open Data File** button.
   The mouse pointer changes to the shape of a finger.
3. Move the mouse pointer to the area where the Fourier-transformed diffusion coefficient measurement data is displayed, and click it.
   The selected diffusion coefficient measurement data is recalled into the **Curve Analysis** window.

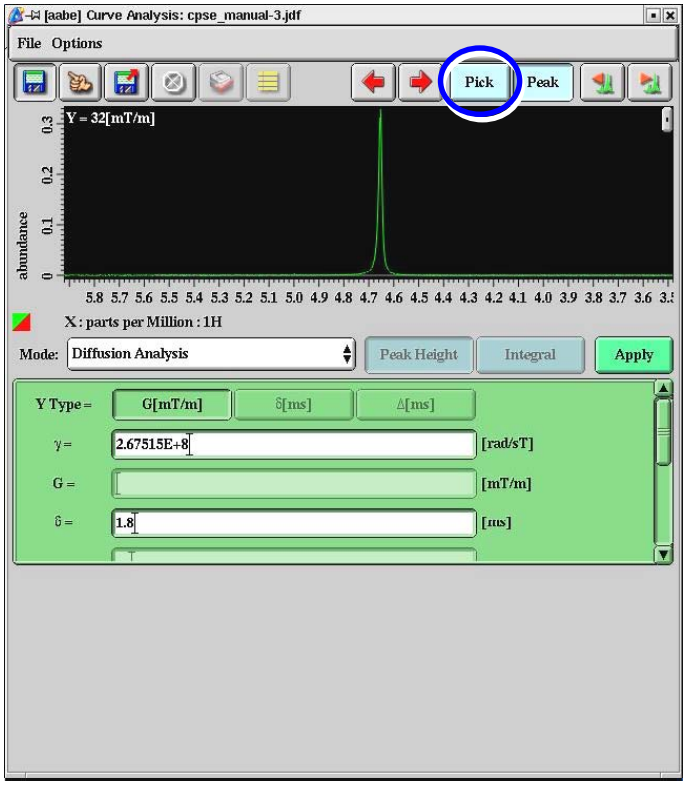
For extracting peak

There are two methods of extracting method of a peak **Pick** mode and **Peak** mode.
If you are using a large number of peaks to calculate the diffusion coefficient, then when printing those diffusion coefficient values collectively, the **Peak** mode is convenient. The candidate peaks of the **Peak** mode should be listed by peak picking beforehand.
Using the **Pick** mode, yuo can measure the diffusion coefficient of an arbitrary peak in a spectrum. It differs from the **Peak** mode, and it is not necessary that the point for calculating the diffusion coefficient is the top of the peak.

- **Method of extracting in Pick mode**

When extracting the peaks in the **Pick** mode, the procedure for creating the peak-intensity table is as explained below.

1. Click on the **Pick** button in the **Curve Analysis** window.
   The cursor tool in the spectrum display range changes to the **Pick** mode.

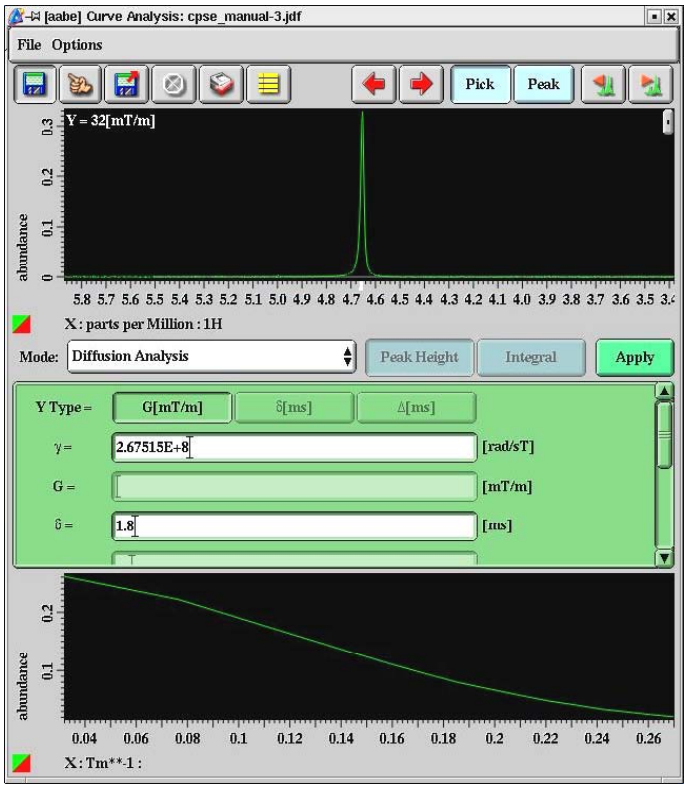


C I

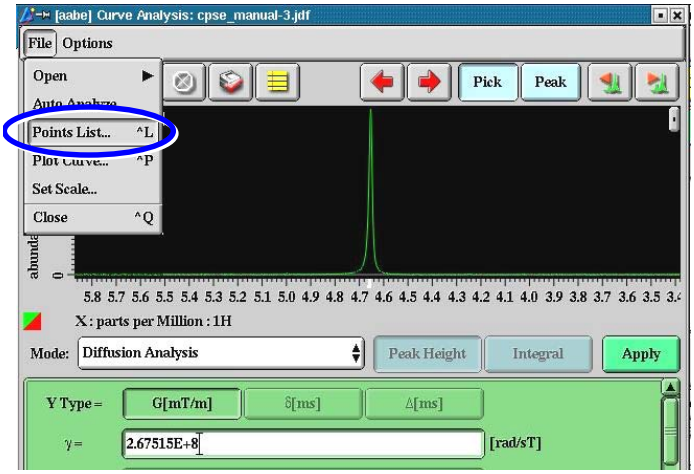
2. Select the **Pick–Pick position** by cursor tool.

3. Move the mouse pointer onto the X ruler in the spectrum display area, and press and hold down the left mouse button.
   A cursor appears.

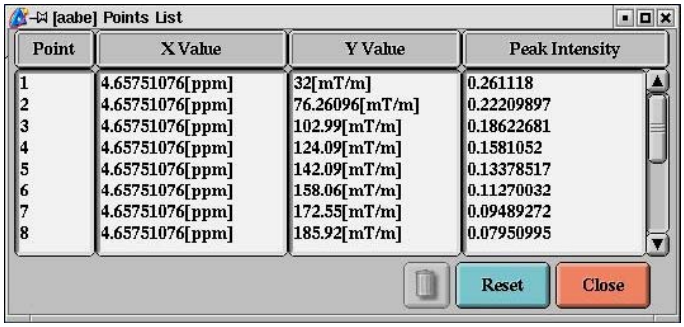
4. While continuing to hold down the left mouse button, move the cursor so that it intersects the top of a peak that you want to use to calculate the diffusion coefficient; then release the mouse button.
   A pick position marker is displayed at the position where you released the mouse button.



5. When displaying the peak-intensity table, select **File–Point List…** in the pull down menu of the **Curve Analysis Tool.**



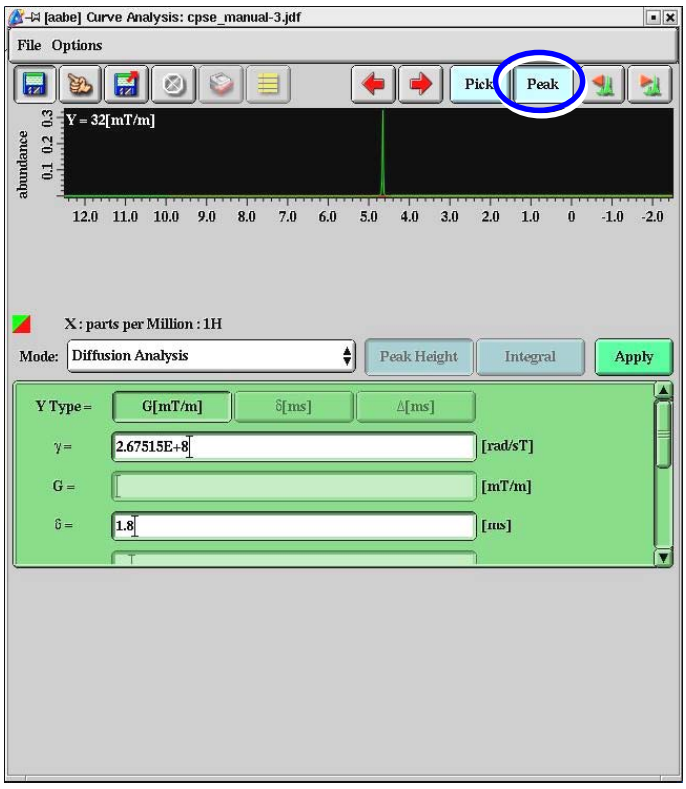
The **Points List** appears.



● Method of extracting Peak in Peak mode

In the **Peak** mode, the procedure for extraction of a peak and creation of a peak-intensity table is as explained below.

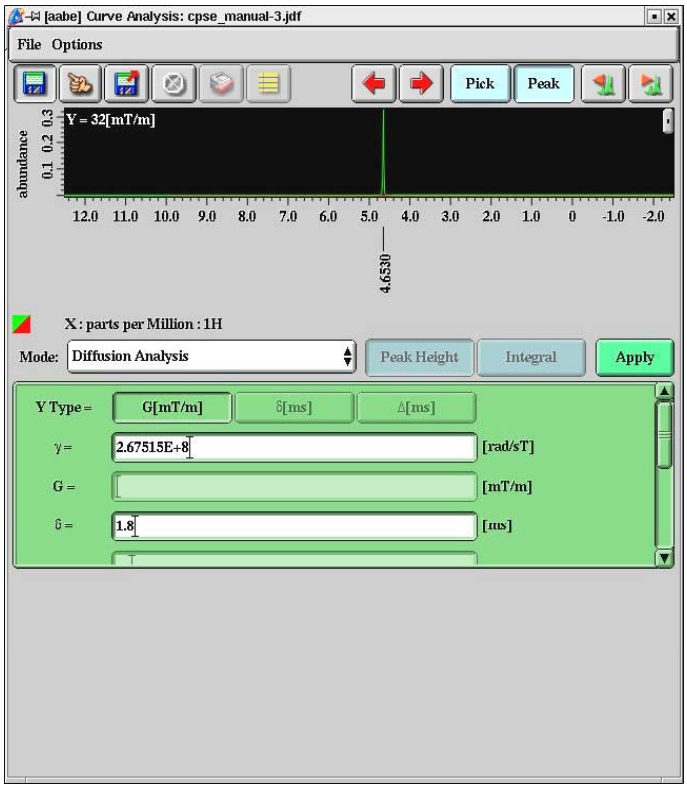
1. Click on the **Peak** button in the **Curve Analysis** window.



2. Click on the **Peak Pick Data** button.

A peak pick is performed.

If necessary, before performing peak picking, adjust the threshold and noise level so that small signals and fine splitting of the peak, which you do not need to obtain the diffusion coefficient, may not be picked.



3. Select **Peak–Select** by cursor tool.

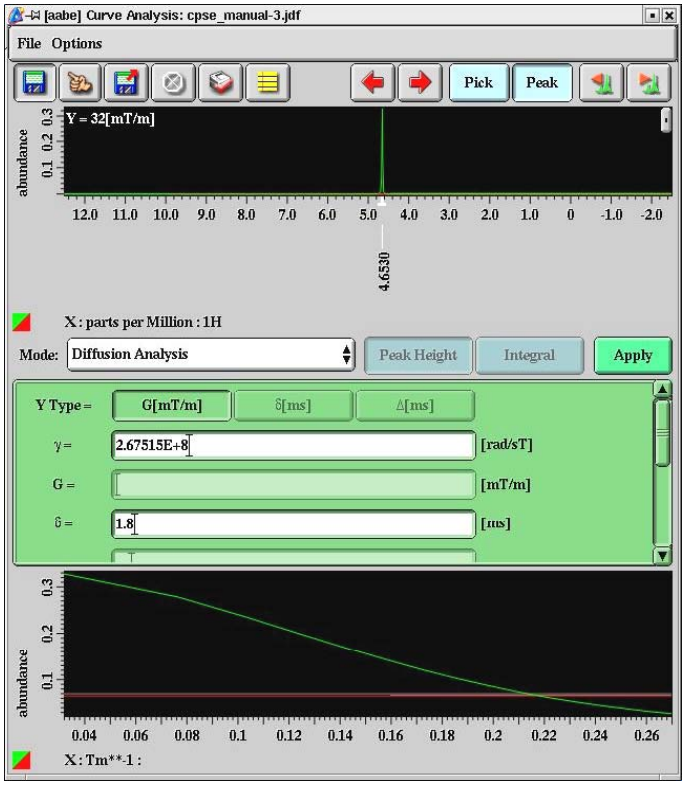
4. Move the mouse pointer onto the X ruler in the spectrum display area, and press and hole down the left button of the mouse.

Cursor appears.

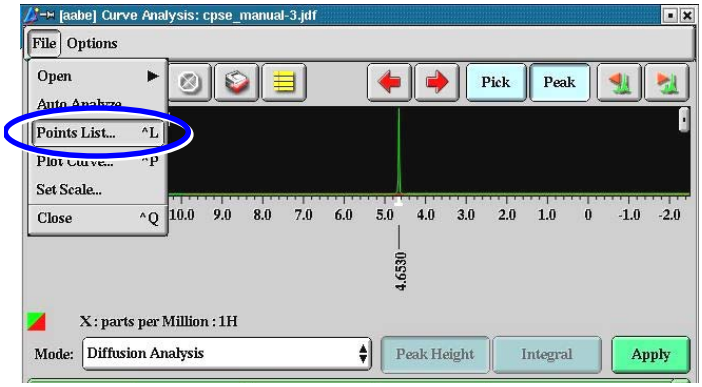
5. While continuing to hold down the left mouse button, move the cursor to the top of a peak that you want to use to calculate the diffusion coefficient; then release the mouse button.

The selected peak changes to white.

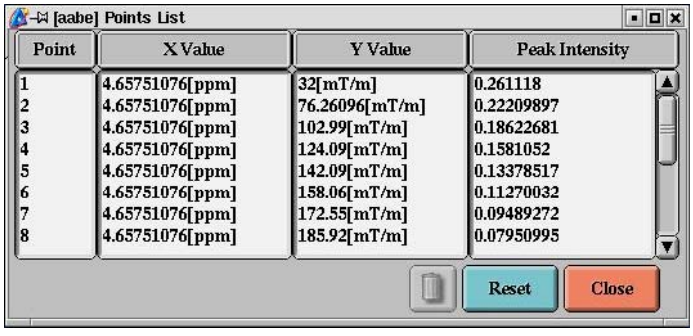
When printing the diffusion coefficient value of two or more peaks collectively, drag the mouse cursor around the area of the peaks. All the peaks listed in the peak-intensity table in the dragged area are selected, and their numerical markers change to white.



6. When displaying the peak-intensity table, select **File–Point List...** in the pull down menu of the **Curve Analysis Tool.**



The **Point list** appears



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2.4.2c Method of obtaining diffusion coefficient by approximate calculation (Step 3)

This method calculates the diffusion coefficient approximately.

■ Input parameters used for measurement

- Select the parameters used as variables for the array measurement in the **Y Value Type** check boxes.

  Enter a check mark into the check box of a variable to selected it.

- Input the gyromagnetic ratio of the nucleus used for calculation and the other parameters which were not used as array variables into the parameter input boxes.

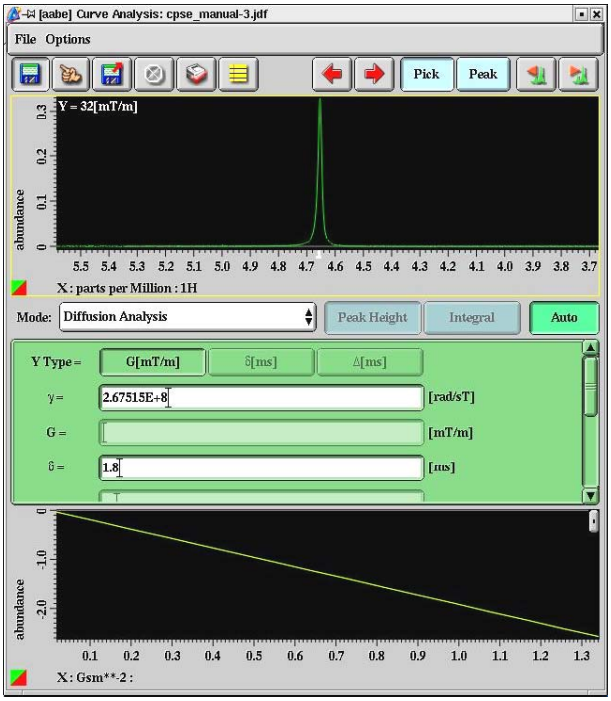
  When the following parameters are used in the used sequence, these default values are read.

γ:	**x_domain**: Gyromagnetic ratio of an observed nucleus
G:	**grad_1_amp** : Amplitude of magnetic-field-gradient pulse
δ:	**delta**: Duration of magnetic-field-gradient pulse
Δ:	**diffusion_time**: Diffusion time

■ To obtain diffusion coefficient by approximate calculation

- Click on the **Apply** button.

  An approximate calculation is performed, and the result of the calculation of a diffusion coefficient and the approximation curve in yellow appear.



When entering in the selection state by pressing the **Apply** button, the display changes to **Auto.** When changing the peak which obtains the diffusion coefficient, or when changing the parameter value, an approximate calculation is performed automatically.

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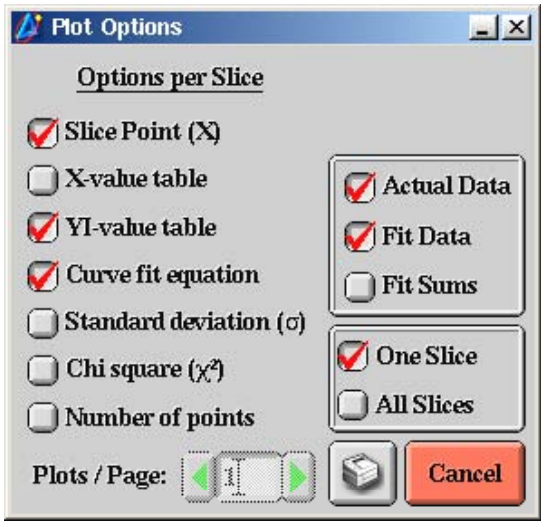
2.4.3 Plotting Calculation Results

1. Click on the **Plot Data File** button in the **Curve Analysis** window.
The **Plot Option** window opens.



2. Place a check mark in the box of each item that you want to plot.
When two or more peaks are selected in the **Peak** mode and you wont to print the diffusion coefficient values of those peaks collectively, turn on **All Slices**.

In order to put check mark on an item to plot, click its button from **Curves & Info, Peaks & Equations** or **Vectors & Equations,** or the check button of an item to plot directly.

3. Click on the **Plot data with current state** icon.
The items selected in step 2 are plotted.

3

DOSY MEASUREMENT AND DATA PROCESSING

3.1 OUTLINE OF DOSY 3-1
3.2 DOSY MEASUREMENT 3-2
3.3 PROCESSING DOSY DATA 3-7
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3.1 OUTLINE OF DOSY

The DOSY (Diffusion-Ordered NMR SpectroscopY) method evolves the diffusion coefficient of a sample on one axis in the two-dimensional spectrum by inverse Laplace transformation or curve fillings.

■ Principle of DOSY

As described in Chapter 2 “Measurement of Diffusion Coefficient and Data Processing", when the phase coherence of the spin is lost due to the first FG pulse and the phase coherence is restored by a second FG pulse, the signal intensity is as follows if interval of two FG pulses is Δ.

$$I(G,\Delta) = I(0,\Delta)\exp(-D(\gamma G\delta)^2(\Delta - \delta/3))$$

Therefore, when two or more NMR signals overlap in the same chemical shift, since the echo intensity becomes a linear combination of the signals, the echo is given as follows.

$$I(G,\Delta) = \sum_{j=I}^{N} I_j(0,\Delta)\exp(-D_j(\gamma G\delta)^2(\Delta - \delta/3)) \qquad (3.1)$$

Moreover, for a sample which has a continuous molecular weight distribution like a polymer, the echo intensity is given as follows.

$$I(G,\Delta) = \int_0^{\infty} G(D)\exp(-D(\gamma G\delta)^2(\Delta - \delta/3))dD \qquad (3.2)$$

where G (D) is the distribution function of D.

Such overlapping signals evolve along with one axis by the diffusion coefficient using the peak intensity. Curve fitting is used for a signal like equation (3.1) and inverse Laplace transformation is used for a signal like equation (3.2).

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3.2 DOSY MEASUREMENT

A DOSY measurement is basically the same as the diffusion coefficient measurement discussed in previous chapter. The only difference between DOSY and diffusion coefficient measurement is that the target of measurement is a multicomponent system or a system having a distribution of molecular weight.

■ To obtain measurement conditions

1. Measure the maximum magnetic-field-gradient intensity of PFG (FG pulse) used measurement.

✍ Refer to Section 2.2 "How to measure PFG strength." for measuring FG pulse strength.

2. Stop the sample spinning, and tune the probe.

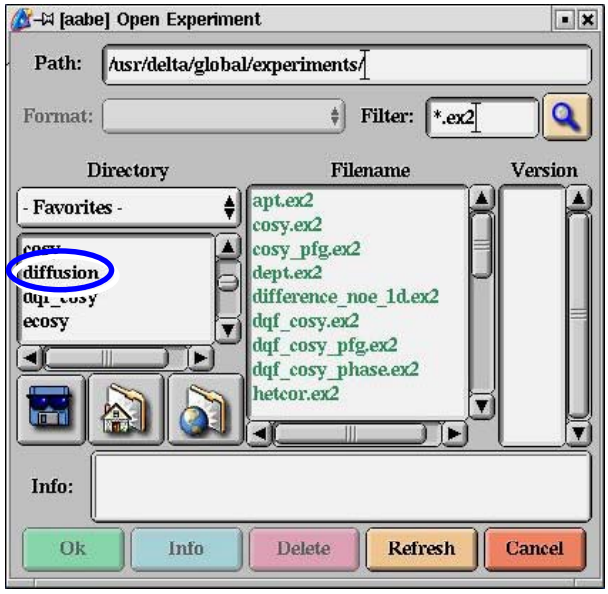
3. Check the 90° pulse width.

✍ In order to improve the accuracy of a diffusion coefficient measurement, we recommend you to check 90° pulse width of the sample to measure. In order to check 90° pulse, perform an array measurement using the measurement mode of **single_pulse.ex2** or **single_pulse_dec.ex2**.

4. Click on the **Expmnt** button in the **Spectrometer Control** window.

The **Open Experiment** window opens.

5. Click on **diffusion**.



6. Select a sequence to use from the File name list box.

The **Experiment Tool** window for setting parameters opens.

7. Input the following values if needed.

For the values of **x_pulse** and **gradient_max** shown in below, the default value in the probe file is automatically called. Input value when the values you found in step 3 differs from the value in the probe file.

x_pulse: 90° pulse width which you obtained in step 3.

gradient_max: The maximum applicable magnetic field strength in the system currently used in [T/m].

✍ For the maximum magnetic field strength to input into **gradient_max**, measure the value for every different combination of the probe and the maximum output of the FG power supply, referring to section 2.2 "How to measure PFG strength".

8. Input values for the parameter of measurement of the diffusion coefficient.

The following three parameters are necessary for measuring the diffusion coefficient

diffusion_time: Time interval of two FG pulses (diffusion time Δ)
grad_1 : Duration of magnetic-field-gradient pulse
grad_1_amp: Magnetic-field-gradient strength (G) [T/m]

✍ The duration of magnetic-field-gradient pulse (δ) for DOSY processing is not equivalent to the parameter **grad_1** in some types of sequence. DOSY processing of Delta program refers to parameter **delta** automatically for duration of the magnetic-field-gradient pulse (δ).

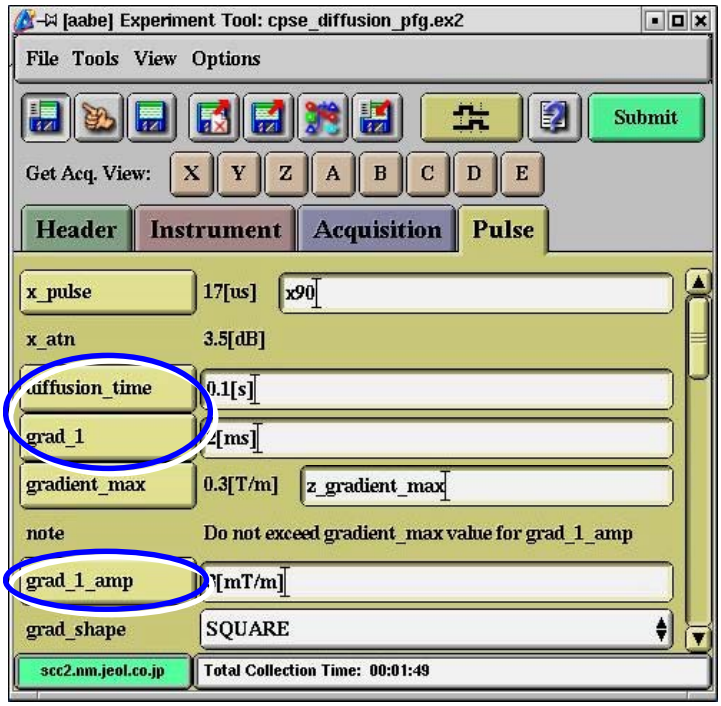


Fig.3.1 Experiment Tool window

9. Input about 10 times the value of T_1 into relaxation_delay.

10. Perform an array measurement at the minimum and maximum value of the variable magnetic-field-gradient strength which are used in the actual measurement.

For example, when changing magnetic field from 3 mT/m to 0.27 T/m, perform an array measurement at 3 mT/m and 0.27 T/m.

✍ A magnetic field strength greater than **gradient_max** cannot be output.

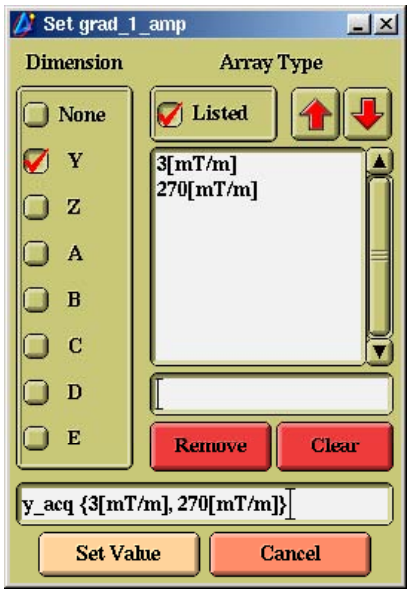


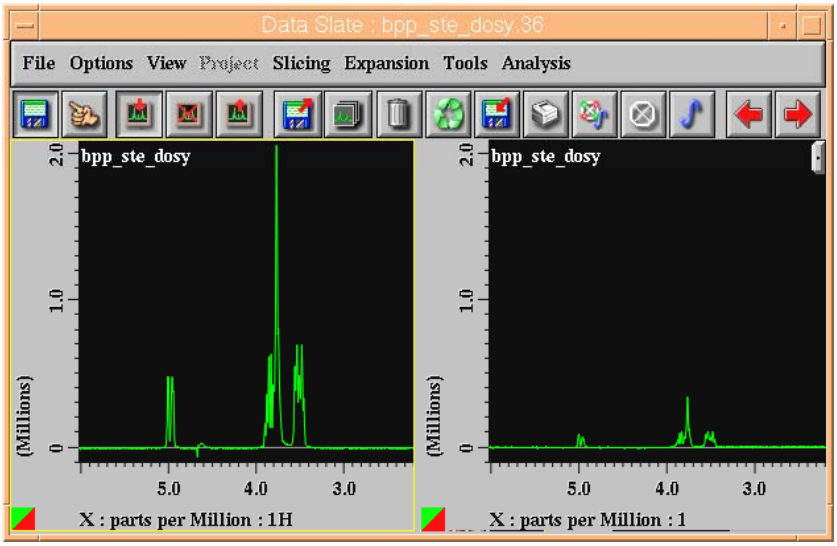
Fig. 3.2 Array parameter window

11. Process the data in the **nD processor** window, and check the decay of the signal.

Be careful of the following points when two or more kinds of molecules are included.

- When the maximum magnetic field gradient to use is applied, adjust measurement conditions so that a signal can be observed also for the molecule with the largest diffusion coefficient.
- Also for the molecule with the smallest diffusion coefficient, select the measurement conditions to make at the decay of the signal intensity about 1/2.

When the measurement sample includes molecules whose the diffusion coefficients different largely, suitable decaying data may not be obtained for each kind of molecule. In this case, we recommend that you divide the measurement sample into a group having a large diffusion coefficient and a group having a small diffusion coefficient, and measure two times under conditions suitable for each group separately.

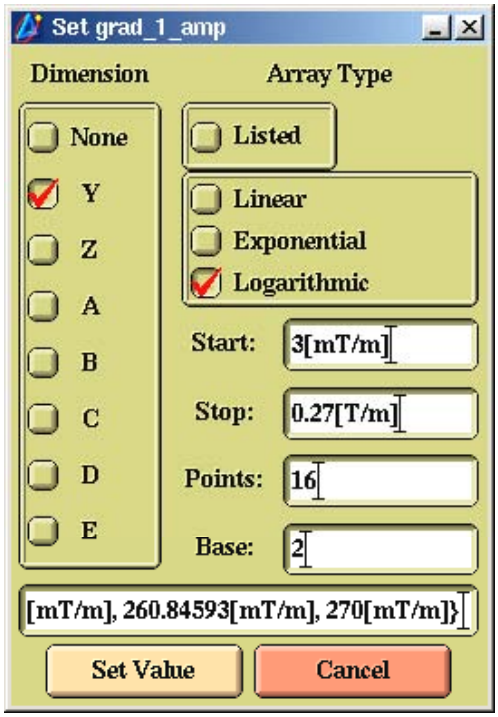


■ DOSY measurement

1. Stop sample spinning, and tune the probe.
2. Check the 90° pulse width.

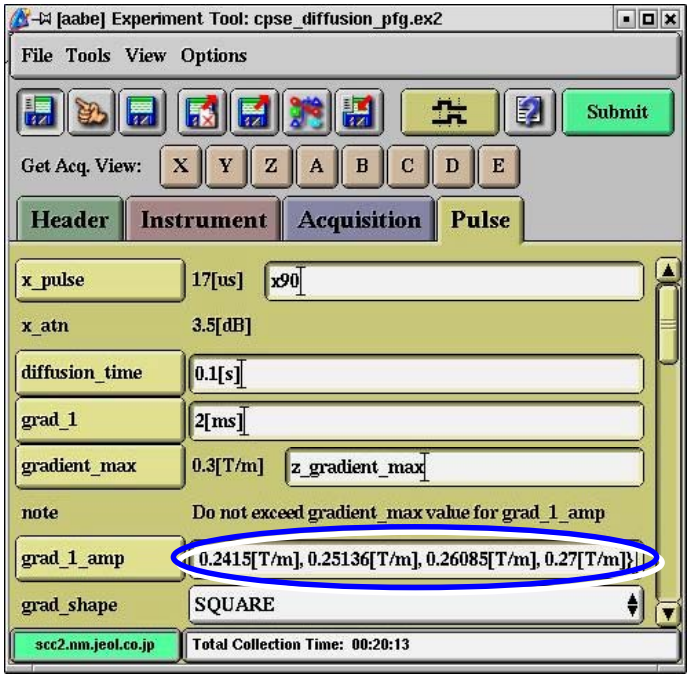
   In order to improve the accuracy of diffusion coefficient measurement, we recommend that you check the 90° pulse width of the measurement sample. In order to check the 90° pulse, perform an array measurement using the measurement mode of **single_pulse.ex2** or **single_pulse_dec.ex2**.
3. Input various parameters obtained by the above procedure "To obtain measurement conditions".

   Set **scans** so that sufficient signal to noise ratio can be obtained for every molecule groups.
4. Set **grad_1_amp** to suitable array variable in the range of the minimum and maximum values of the variable magnetic-field-gradient which were used in condition setting.



5. Click on the **Set Value** button.

   Close the array parameter window, and input the settings into **Experiment Tool** window.



6. Click on the **Submit** button.
Measurement starts.

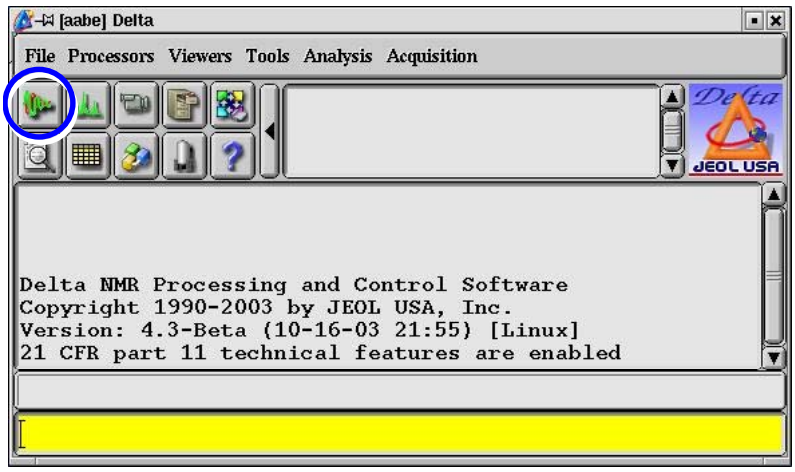
3.3 PROCESSING DOSY DATA

After measurement process the data in the nD Processor window.
First, measurement data are loaded into the **nD Processor** window as in two-dimensional measurement data processing. In addition, when the measurement data is transmitted from the spectrometer immediately after the end of DOSY measurement and the **nD Processor** window is already open, the operation of section 3.3.1 is not necessary.

3.3.1 Reading DOSY Measurement Data

In order to load the data (FID) of DOSY measurement into the **nD Processor** window, perform the following procedure.

1. Click on the **Data Processor** button in the **Delta Console** window.


[aabe] Delta
File Processors Viewers Tools Analysis Acquisition
JEOL USA
Delta NMR Processing and Control Software
Copyright 1990-2003 by JEOL USA, Inc.
Version: 4.3-Beta (10-16-03 21:55) [Linux]
21 CFR part 11 technical features are enabled

The **Open Data for Processing** window appears.

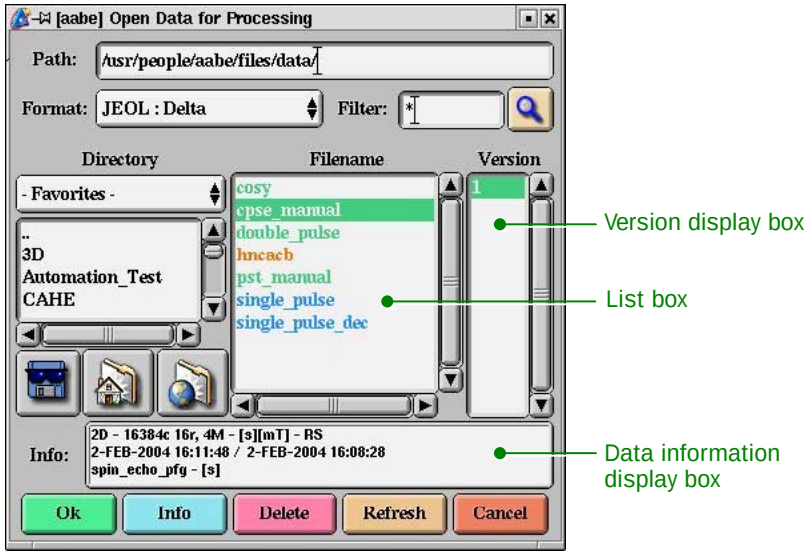
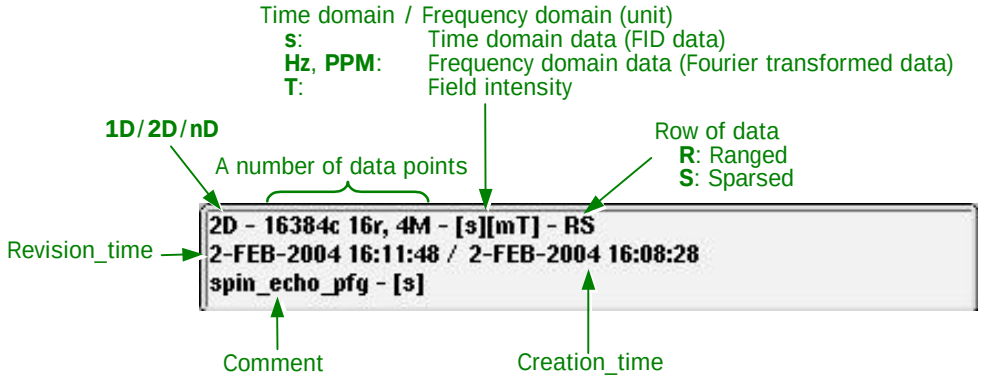


Fig. 3.3 Open Data for Processing window

2. Click the data file called from the list box.

The data information on the newest version is displayed in the data information display box as shown below. Note that the format of the data obtained by the array measurement is displayed as 2D data.



3. Looking at the data domain of the data information display box, and select the version of stored FID from the version display box.

If the newest version of the data displayed in step 2 is the time domain data, selection of the version is unnecessary.

4. Click on the **Ok** button.

nD Processor window opens.

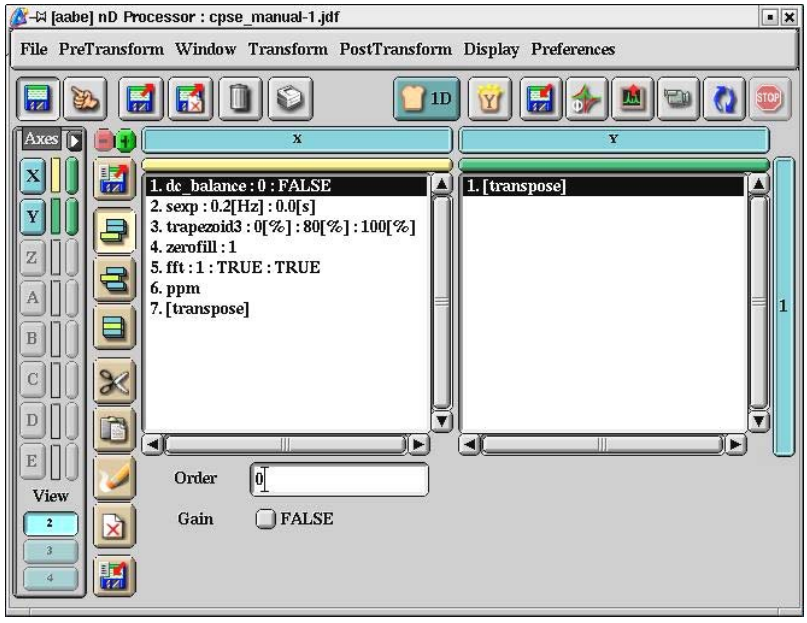


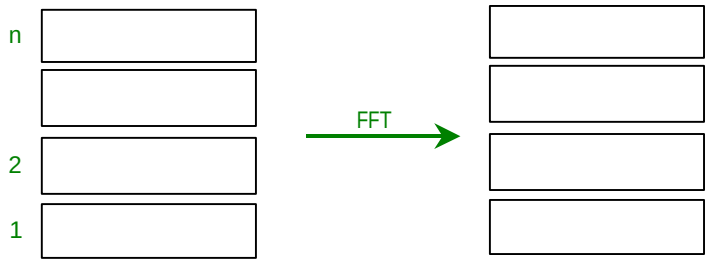
Fig. 3.4 nD Processor window

3.3.2 Procedure for Processing DOSY Measurement Data

The processing of the DOSY measurement data consists of the following two steps.

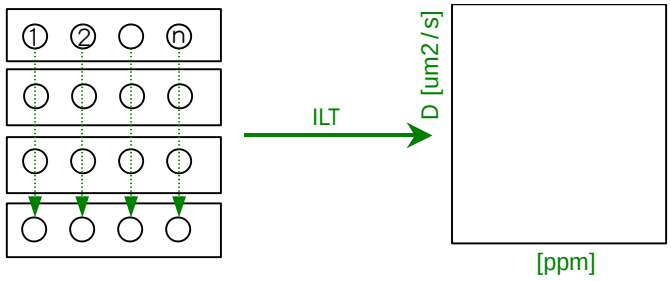
Step 1

Fourier transformation the X-axis of DOSY measurement data set under same conditions for the 1 to n-th measurement data set as shown in the following schematic diagram.



Step 2

For the processing of the Y-axis of DOSY measurement data, Inverse Laplace Transformation is carried out on every data point that is Fourier transformed along the X-axis as shown in the following schematic diagram.



The procedures are explained in the order of these steps below.

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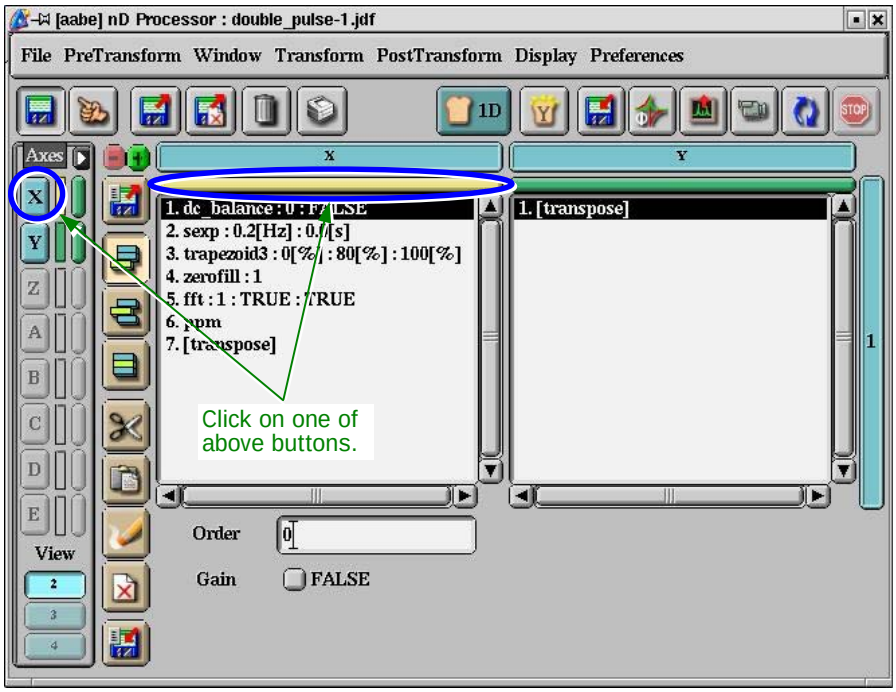
3.3.2a Processing for x-axis of DOSY measurement data (Step 1)

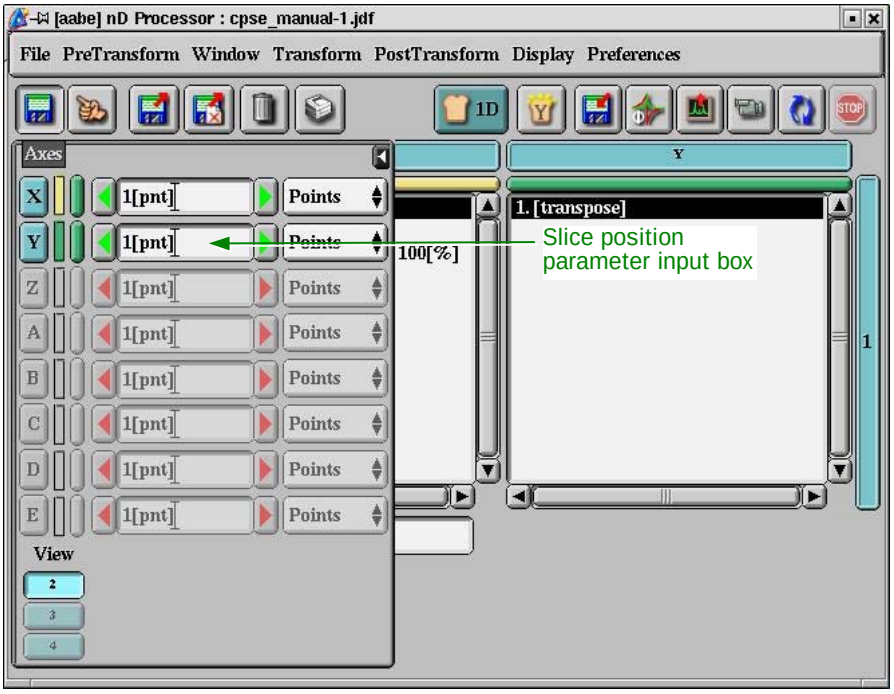
Display one data of DOSY measurement data in the **1D Processor** window as 1D slice data, and search a suitable window function and phase correction values.

1. Click on the **X** button in the **nD Processor** window.



2. Click on the **Axes** button to display the slice position setting screen, and set the slice data to the number of points from the number of sets (1 - n) in the DOSY measurement data.

Usually, slice the first measurement data whose phase correction is easy to performed.



3. Click on the 1D Slice **1D Slice** button.

The slice data at the specified position is displayed in the **1D Processor** window.

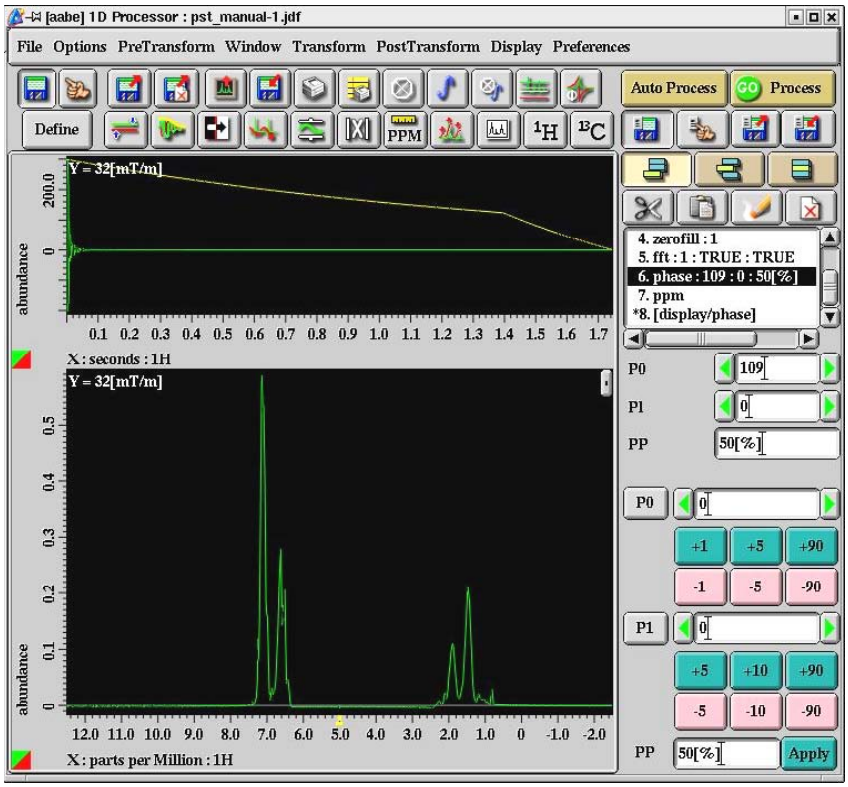


Fig.3.5 1D Processor window

4. Changing the window function and parameter value, set up suitable window function conditions.

The operation of changing the window function is the same as that of usual 1D data. The height information of a peak is required for inverse Laplace transformation of DOSY. Therefore, in order to reduce the contribution of noise, it is more effective to use a larger window function conditions than usual data processing.

5. Correct a phase manually, and obtain suitable phase correction values.

The phase correction is the same as that of the usual 1D data.

- Be sure to perform phase correction manually without using automatic phase correction.
- A phase may not correct at the peak having J coupling due to J modulation. If that happens, refer to section 2.4.2 "Reference: When the phase of measurement data can not be corrected."

6. Close the 1D Processor window.

The window function conditions and phase correction value, which were obtained in steps 4 and 5, are automatically entered in the process list in the **nD Processor** window.

7. Select **Post Transform–Math–Real** from the menu bar.

Real processing is sentered in the process list of windows.

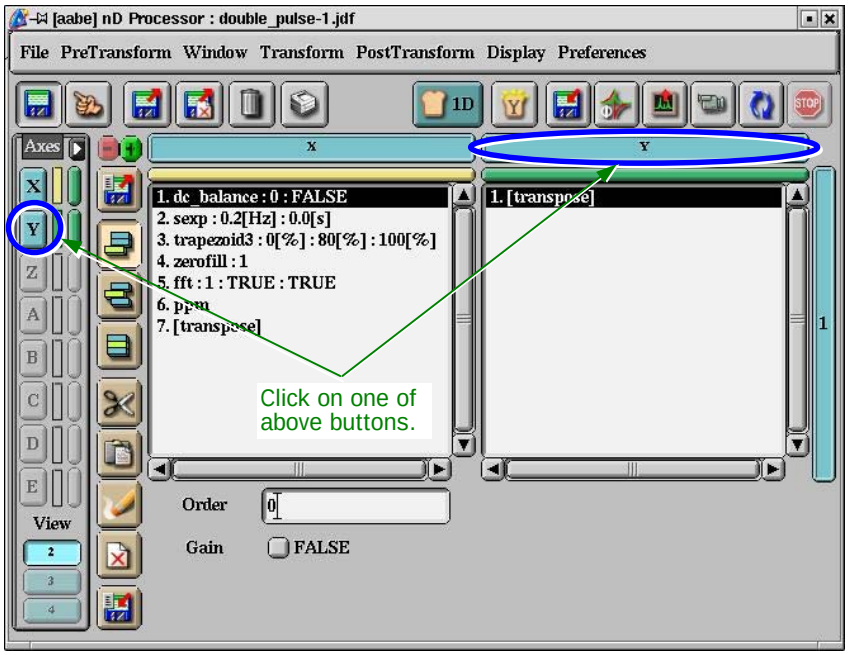
- In inverse Laplace transformation processing of DOSY, only real data is need.

C I

3.3.2b Processing for y-axis of DOSY measurement data (Step 2)

Carry out inverse Laplace transformation of the Y-axis for the data Fourier transformed in the direction of the X-axis in step 1.

1. Click on the **Y** button in the **nD Processor** window.



2. Select **Transform–DOSY** in the menu bar, and select the algorithm used for processing.

3. Set up the various parameters.

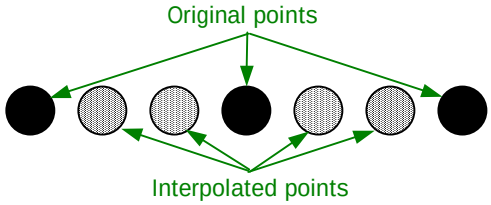
There are the following parameters.

In the **nD Processor** window, only three parameters are displayed simultaneously. When the parameters you want to change are not displayed, display them by clicking the **Back to previous parameter group** button or the **Advance to next parameter group** button.

Start: This is the minimum value of the range over which to search for the peak to use to measure the diffusion coefficient.

Stop: This is the maximum value of the range over which to search for the peak to use to measure the diffusion coefficient.

Interp: This determines the number of points to interpolate in the diffusion coefficient axis (Y-axis).
Example: When the number of data points is three, and **Interp** is 2, thenumber of points becomes 7 after processing.



In the CONTIN method, values of **Interp** that are 15 or more are suitable.

Threshold: Threshold level of the peak to used for processing.
When **Threshold** is 0, the default value of Delta software is used.

Species: Set the total number of components expected.

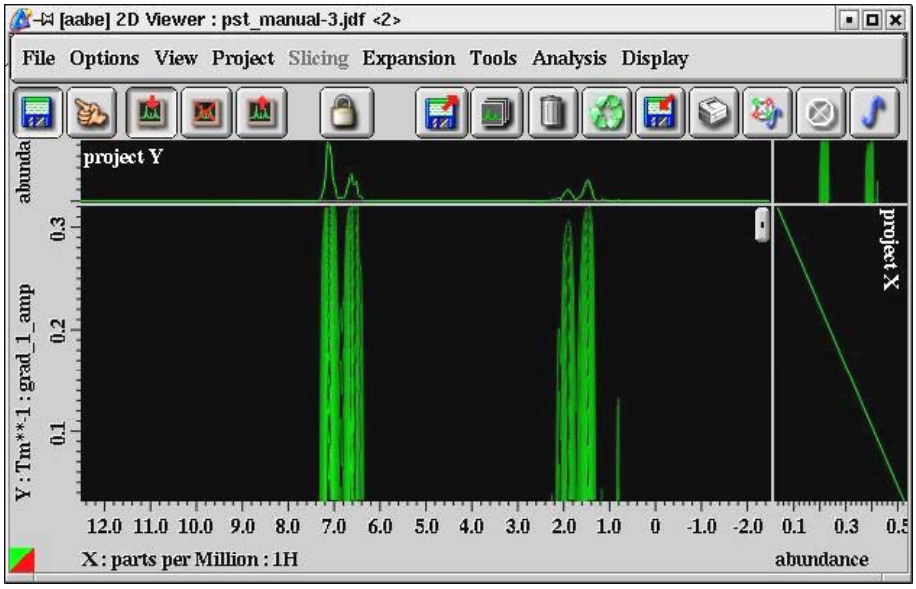
Peaks: Set this to the maximum number of the diffusion coefficient expected for each chemical shift.
In the L-Marquardt method, set **Peaks** to 1.

Ratio: In the SPLMOD method, set this to the minimum ratio of the different diffusion coefficients having equal chemical shift.
This parameter applies only to the SPLMOD method.

Error: Set this to the permissible error in the SPLMOD method as decimal.
Example: When **Error** is 0.2, the permissible error is 20%.
this parameter applies only to the SPLMOD method.

Gamma: Set this to the gyromagnetic ratio of the nucleus used for processing.

4. Click on the **Process File And Put In Data Viewer** button.
Data processing is performed, and DOSY data is displayed.


[aabe] 2D Viewer : pst_manual-3.jdf <2>
File Options View Project Slicing Expansion Tools Analysis Display
project Y
project X
abunda
0.3
0.2
0.1
Y : Tm**-1 : grad_1_amp
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0 0.1 0.3 0.5
X : parts per Million : 1H
abundance

5. Repeating steps 3 and 4, obtain the search condition for the diffusion coefficient in the suitable range.

- **Logarithmic display of diffusion coefficient axis.**

In the diffusion coefficient axis, logarithmic display may be more legible. Here, the procedure for logarithmic display is explained.

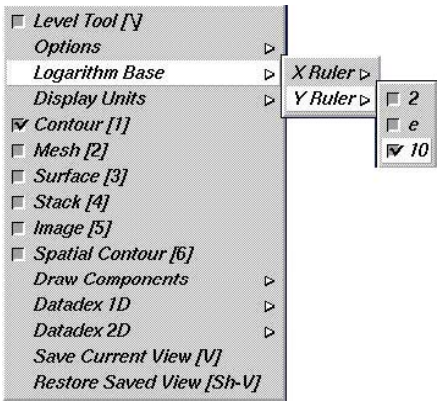
1. Set cursor tool to **Select geometry** in **Select** mode, and click on DOSY data display area on the screen.
The DOSY data display range is selected.

2. Right click in the data display area.
A pop-up menu appears.

C I

3. Select the bases of the logarithm from **Logarithm Base–Y Ruler of the** pop-up menu.

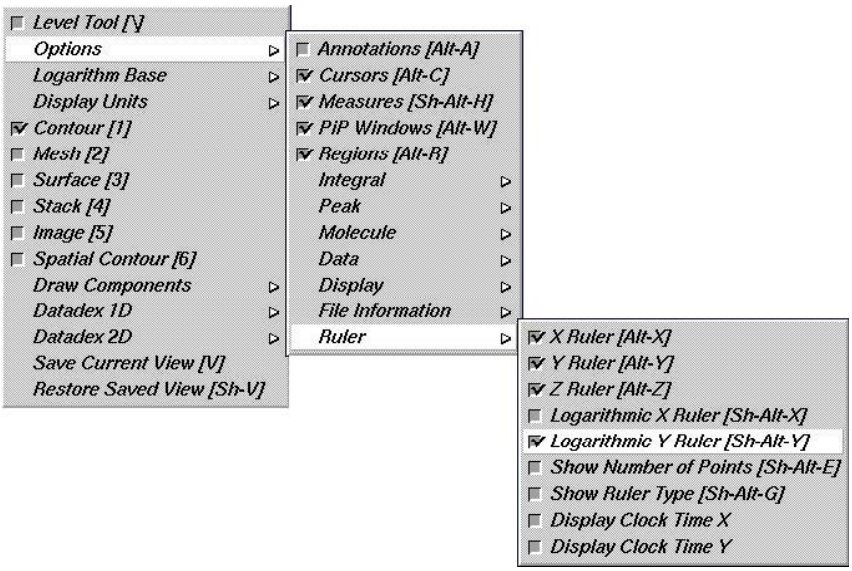
The base can be selected from **2** and **10** for common logarithms, and **e** for natural logarithm.



4. Right click in the data display area again.

A pop-up menu appears.

5. Select **Options–Ruler–Logarithmic Y Ruler** from the pop-up menu.



The Y-axis changes to logarithmic display.

4

MEASUREMENT OF SR-MAS

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4.3 ADJUSTMENT OF RESOLUTION 4-4
4.4 ADJUSTING TUNING 4-6
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4.1 OUTLINE OF SR-MAS MEASUREMENT

SR-MAS (Swollen Resin Magic Angle Spinning) is a measurement method for gel samples, swollen resin of solid phase synthesis, and heterogeneous systems such as tissue. In order to perform this measurement, it is necessary to use the special SR-MAS probe which can carry out MAS measurement and the special-purpose sample tube use for liquid samples which does not leak even if it rotates at several kilohertz.

☞ Refer to the manual of the SR-MAS for the preparation and the operation of the SR-MAS probe.

The pulse sequence used for a SR-MAS measurement is the same sequence as the pulse sequence used for general solution NMR measurement. Therefore, the basic measuring method and data-processing method are the same as those of solution NMR.

✍ However, the pulse sequence using field gradient (FG) cannot be used.

Here, the method of adjustment of the magic angle, the resolution and tuning, the temperature controlling, and the relationship between spinning speed and resolution, that is peculiar to the SR-MAS NMR measurement and different from the general solution NMR measurement in the spectrometer, are explained.

■ SR-MAS measurement

SR-MAS is the abbreviation of Swollen Resin Magic Angle Spinning. It means that the resin swallenby the solvent is directly measured under the condition of several-kilohertz MAS spinning. The resolution of the spectrum of semisolids (soft solid) and high-viscosity liquids will be improved by reducing the residual weak dipole-dipole interaction of a sample by MAS. Moreover, higher resolution can be reached by averaging inhomogeneity of the local magnetic field around the rotating axis.

— CAUTION ————

Be sure to rotate a sample in SR-MAS experiment. If you measure without the air for sample spinning flowing, the probe may be damaged. However, when you carry out the resolution adjustment using single_pulse.ex2, damage to the probe does not occur even if a measurement is carried out without air flowing.

C I

4.2 HOW TO ADJUST MAGIC ANGLE

— CAUTION ————

Receive instruction from an experienced person when the magic angle is adjusted the first time. The SR-MAS probe may be damaged if unsuitable adjustment is performed.

1. Insert the reference sample KBr.
2. Start the spinning.
3. Insert the stick for magic-angle adjustment through the top of the SCM.
4. Change LF (Lower frequency) channel to **Bromine79** observation.

   Check the combination of the stick and the tuning dial for Bromine79 observation.
5. Load the pulse sequence **global/experiments/single_pulse.ex2** in the **Experiment Tool** window, and perform the following setting.
   - Set observed nucleus to **Bromine79**.
   - Set **x_sweep** to 1000 ppm.
   - Add the repeat flag to Header, and turn on spinning.
   - Set **scans** to **1**.
6. Click on the **Submit** button.

   The pulse occurs, and measurement starts.

   If the **Inform** window appears, click on the **GO** button.
7. Adjusts a phase by the following procedure.
   a. Click on the **View** button.

      The ***View Tool*** window opens.

   b. After clicking on the **View** button, click on the **Process vector** button to change the display.

   c. Select **Processing**–**Phase** and **Processing**–**Phase Boxes.**

      The **Phase Boxes** window opens.

   d. Adjust the phase.
8. Adjust the magic angle.

   Turn the adjustment stick to maximize the spinning side band of KBr (Fig. 4.1) .

   The gear of the magic-angle adjustment mechanism has some backlash. Therefore, adjust it by turning the dial for fine-tuning in only one direction.

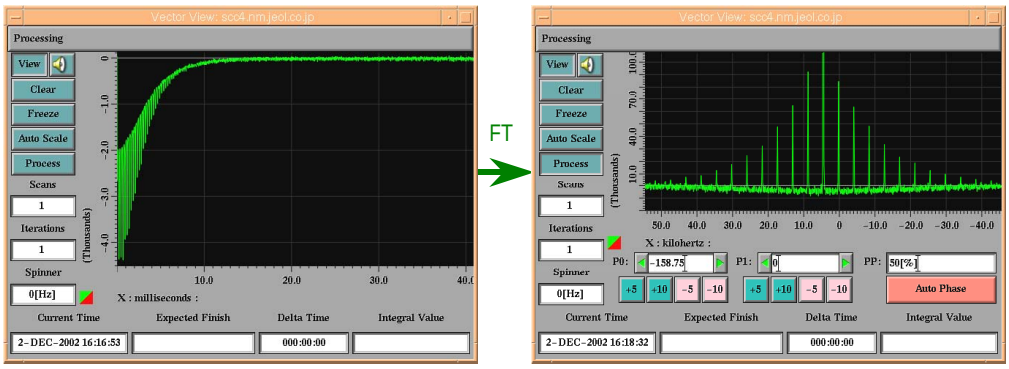


Fig 4.1 Free Induction Decay (left) and spectrum (right) after magic-angle adjustment

C I

9. After completing magic-angle adjustment, select the current measurement in the **Spectrometer Control** window, and click on the **STOP** button.

✍ If a measurement is stopped while it is in progress, the data file is stored automatically, and the version of the data file increases. In order to keep space free on the hard disk, delete the file at any time.

10. Remove the stick for adjustment.

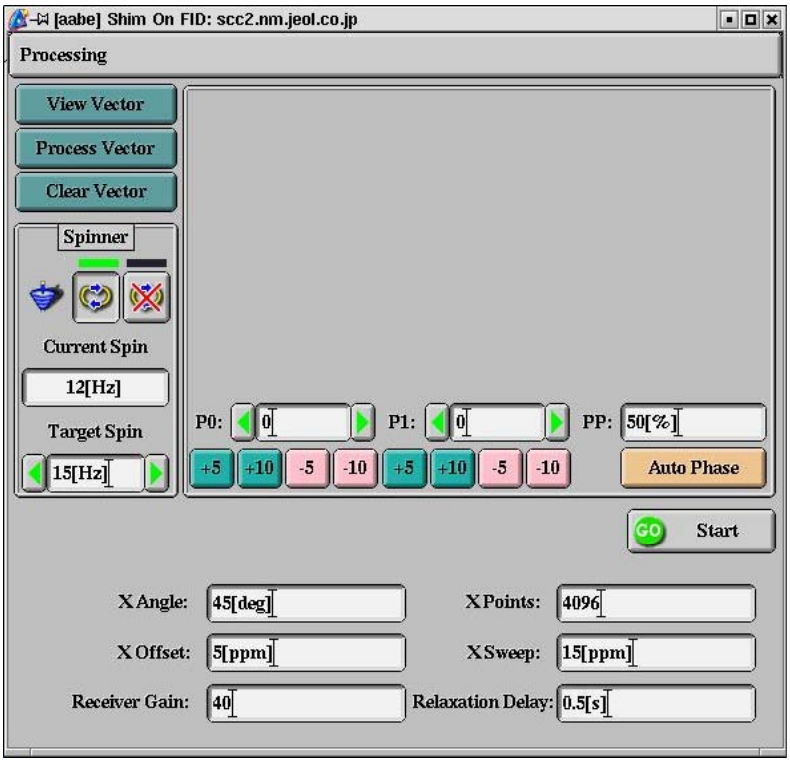
✍ Adjustment of the magic angle may change the resolution. Be sure to check the resolution according to section 4.3 "Adjustment of resolution", and adjust the shim values if needed.

C I

4.3 ADJUSTMENT OF RESOLUTION

1. Insert the chloroform ($CHCl_3$)sample.
It is not necessary to perform spinning.

2. Select **Config–Shim on FID** in the pull down menu of the **Spectrometer Control** window.



3. Click on the **Start** button.
The spectrum is updated continuously.

4. Adjust the phase.

5. Expand near the peak, and check the resolution.

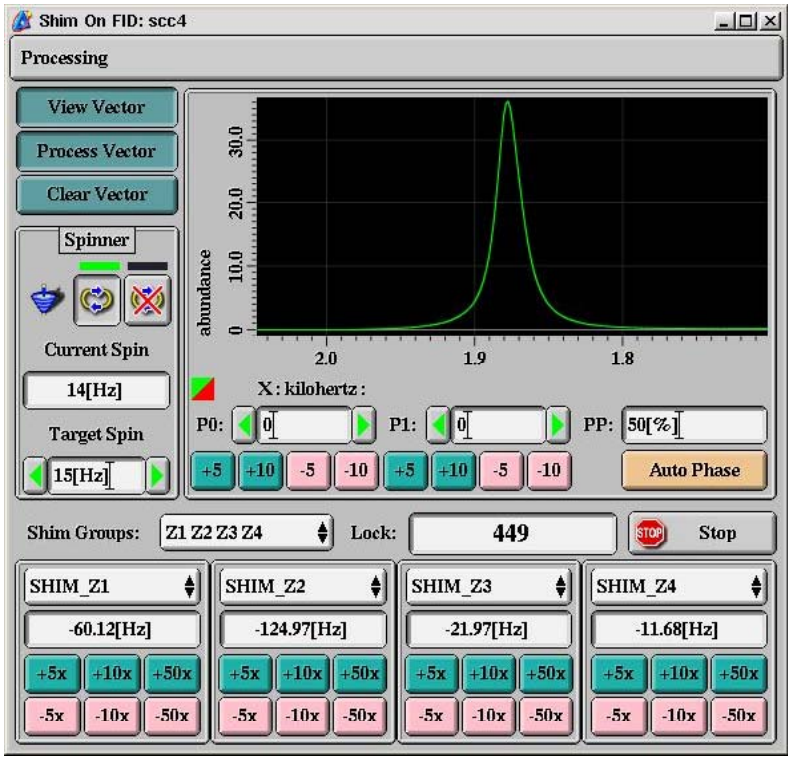


Fig. 4.2 View Tool window in resolution adjustment

6. If the resolution is not good, adjust the resolution as followings
   a. Open the **Sample** window, and adjust **Z1** to maximize the peak intensity.
   b. Adjust **X2** and **Y2** to maximize the peak intensity.
   c. Adjust **Y** and other axes to maximize peak intensity.
   d. Repeat steps a to c.
7. Click on the **STOP** button after shim adjustment is complete.

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4.4 ADJUSTING TUNING

In order to apply RF pulses to a sample efficiently, tuning is necessary operation. If tuning shifts, measurement conditions will change, and the S/N ratio of the spectrum will decrease. Furthermore, if tuning shifts greatly, it will cause electric discharge in the probe.

4.4.1 When Tuning is Necessary

Tune the probe in the following cases. Perform the measurement under the best conditions of both the observation and the irradiation system.

■ When an observed nucleus is changed

Tuning of the observation and irradiation system is necessary.

The stick selection and the standard position on the dial scale of major nuclei are indicated in the table supplied with the probe. When the observed nucleus is changed, estimate the tuning point roughly with the numerical value from the table, and then fine-tune.

■ When the sample is changed

Although the tuning and matching of the observation system hardly change for an ordinary sample unless VT measurement is performed, the tuning of the irradiation system changes a little.

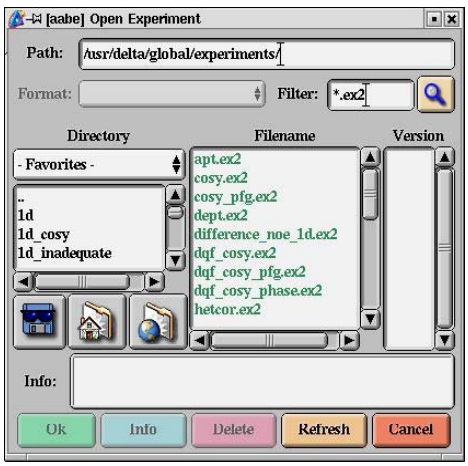
For a sample with a high dielectric constant or a semiconductor sample, tuning and matching of the irradiation and observation system change sharply. Be sure to tune the probe.

4.4.2 How to Tune

After inserting the sample and setting the sample spinning speed, tune according to the following procedure. Here, as an example, the case ic which the measurement method is **single_pulse_dec,** the observed nucleus is Carbon13 and the irradiation nucleus is Proton will be introduced.

1. Click on the **Expmnt** button in the **Delta Console** window.

The **Open Experiment** window opens.



C I

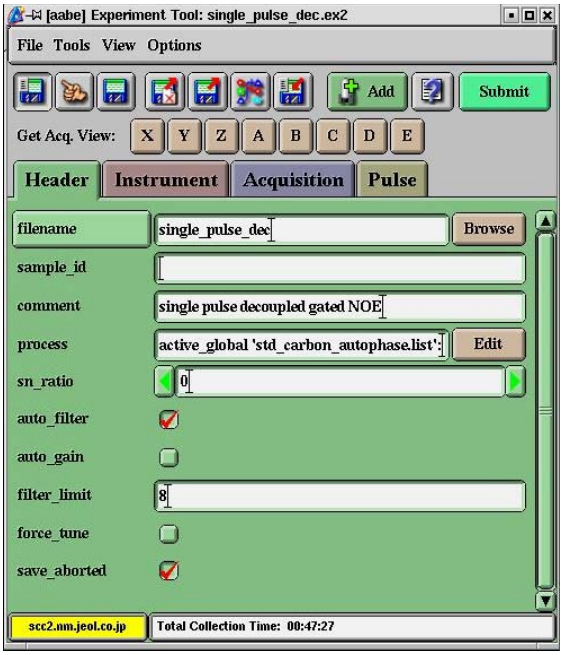
2. Click on the button.

The contents of the **Global Experiment** directory appear.

a. Click on the measurement mode **single_pulse_dec.exp**, and highlighting it.

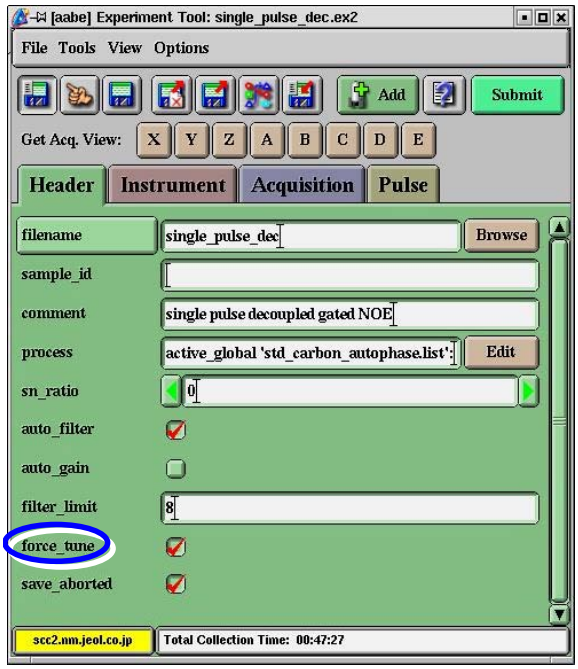
b. Click on the **OK** button.

The **Experiment Tool** window opens.



3. Enter the measurement conditions in the order of **Header, Instrument, Acquisition** and **Pulse** in the **Experiment Tool** window.

4. Click on **force_tune** in the **Header**.



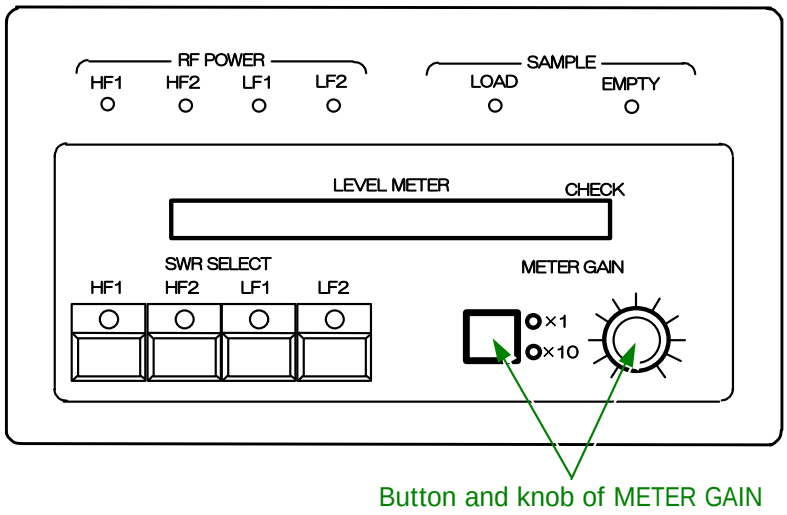
C I

5. Click on the **Submit** button.

A tuning message appears. The message of Proton appears first. At this time, the NMR system is already prepared for tuning.

6. Adjust the sensitivity of the indicator for Proton tuning.

If LEVEL METER of the head amplifier chassis is out of range, or does not move far, adjust the button and knob of METER GAIN.



7. Adjust HF (high frequency) TUNE knob of the probe to minimize LEVEL METER display first, and next, adjust the HF MATCH knob. Finally adjust the HF TUNE knob again.

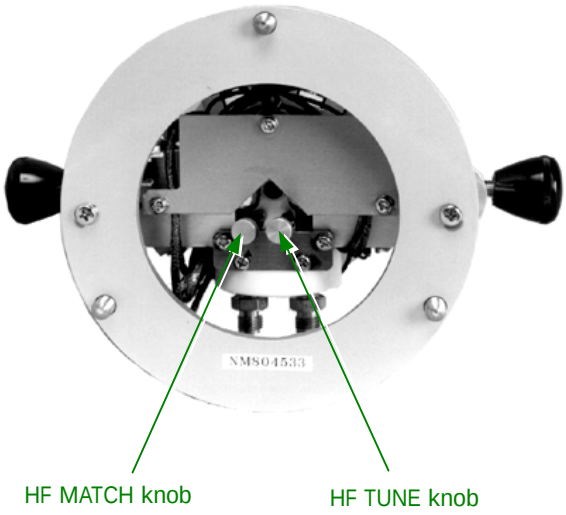
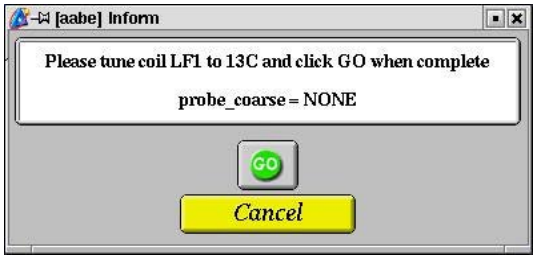


Fig. 4.3 Bottom view of the probe

8. When tuning of Proton is complete, click on the **GO** button.

Then, the message of Carbon13 appears. At this time, the NMR system is already prepared for tuning.



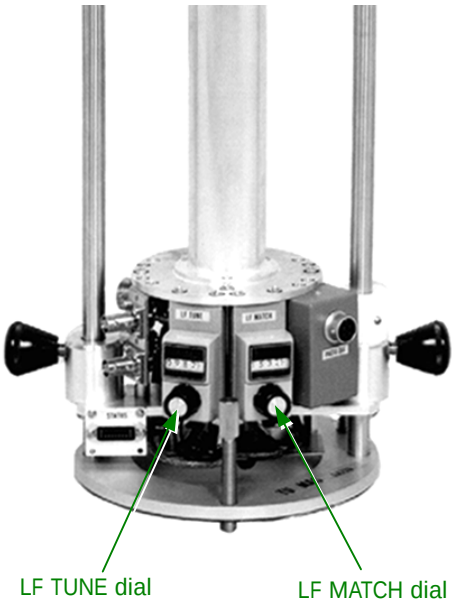
9. Adjust the sensitivity of indicator for Carbon13 tuning.

If LEVEL METER of the head amplifier chassis is out of range, or does not move far, adjust the button and knob of METER GAIN.

10. Check that no stick is attached for Carbon13.

In nuclei other than Carbon13, since there are nuclei that need a stick, refer to the data provided at delivery time.

11. Adjust the LF TUNE dial of the probe first to minimize the LEVEL METER display, and next, adjust the LF MATCH dial. Adjust the LF TUNE dial and LF MATCH dial several times to minimize LEVEL METER reading.



When adjusting tuning precisely, refer to section 4.4.3 "How to adjust tuning precisely for Carbon13".

12. When the tuning is complete, click on the **GO** button.

The ordinary measurement of Carbon13 starts.

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4.4.3 How to Adjust Tuning Precisely for Carbon13

1. Turn the LF MATCH dial to minimize the deflection of LEVEL METER.
2. Turn the LF TUNE dial to minimize the deflection of LEVEL METER.
   Make a note of the deflection (F1) of LEVEL METER at this time.
3. Turn the LF MATCH dial to the +10 mark, and turn the LF TUNE dial to minimize the deflection (F2) of LEVEL METER.
   Compare the deflection (F2) of LEVEL METER at this time with F1.
   Repeat the above steps until the deflection of LEVEL METER becomes the minimum.

4.5 TEMPERATURE CONTROL

For the SR-MAS probe, the temperature can be controlled in the range from room temperature to +50 ℃. The temperature control can be carried out in the same way in the usual solution NMR measurement. However, perform temperature control with the air for sample spinning flowing in any case.

— CAUTION ————

If a variable-temperature experiment is performed while sample air is not flowing, the probe may be damaged.

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4.6 SPINNING SPEED AND RESOLUTION

In some sample systems, the resolution changes when the spinning speed changes. For such a sample system, adjust the spinning speed to optimize the resolution.

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